

UNIVERSITE DE GENEVE
Département de Chimie
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FACULTE DES SCIENCES
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**A STUDY OF THE STABILITY OF SOME
COMPLEXES OF PALLADIUM (II)**

THESE

présentée à la Faculté des Sciences
de l'Université de Genève
pour obtenir le grade de docteur ès sciences chimiques

par

Vanaja PARTHASARATHY
de l'Inde

Thèse No 1742

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A STUDY OF THE STAMINATE
COMPLEX OF *CALLUNA* III

1932

Prof. Dr. J. van der Pijl

at the University of Groningen

and Dr. J. van der Pijl at the University of Groningen



La faculté des sciences, sur le préavis de
Messieurs C.K. Jørgensen, professeur ordinaire
et directeur de thèse, et E.A.C. Lucken,
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les propositions qui y sont énoncées.

Genève, le 12 avril 1976

Thèse No 1742

Le doyen :
J. Müller

ACKNOWLEDGEMENT

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and helpful suggestions in carrying out this work.

RESUME

Dans ce travail on a étudié l'influence de la 1,10- phénanthroline fortement liée sur la stabilité des ligands A_2 dans les complexes $[Pd(phen)A_2]^{2+}$. On a déterminé les constantes de formation de A dans $[Pd(phen)A_2]^{2+}$ où A = ammoniacque, pyridine; $A = 1$ 'éthylènediamine (1, 2 -diaminoéthane), 1,10- phénanthroline $^{2-}$ et de X dans $[Pd(phen)X_2]$ où X = chlorure, bromure et hydroxyle.

Les mesures des constantes de stabilité ont été effectuées par potentiométrie (mesures de pH), spectrophotométrie et conductimétrie.

Comme les constantes de formation étudiées sont assez élevées et séparées, on a utilisé la méthode classique de Bjerrum pour les évaluer. Le résultat le plus surprenant est la formation d'un anion pentacoordiné, $[Pd(phen)(OH)_3]^-$ avec $\log K_3 = 4.4$. La faible stabilité ($\log K_2 = 9.4$) pour la phénanthroline quand on la compare avec l'éthylènediamine ($\log K_2 = 17.8$) est une indication de la tension considérable présente dans $[Pd(phen)_2]^{2+}$. On a constaté que l'ion diaquophénanthroline palladium (II), $[Pd(phen)(H_2O)_2]^{2+}$ est assez acide avec un $pK_a = 3.3$.

On a aussi observé que la formation de $[Pd(phen)_2]^{2+}$ et $[Pd(phen)en]^{2+}$ est lente (de quelques minutes à plusieurs heures) et, en conséquence, une étude cinétique de ces réactions a été faite.

On a enfin déterminé les spectres dans l'ultra-violet de quelques-uns des complexes mentionnés ci-dessus.

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LIST OF ABBREVIATIONS

py	pyridine
en	ethylenediamine (1,2-diaminoethane)
dmg	dimethylglyoxime
dip	dipyridyl
phen	1,10-phenanthroline (ortho-phenanthroline)
terpy	terpyridyl
dien	diethylenetriamine

CHAPTER I

INTRODUCTION

Inorganic complexes, especially transition metal complexes have fascinated chemists from the early stage of their discovery because of their striking colours and their unusual magnetic properties and in more recent years because of the varying nature of their bonding which they display from the most covalent type (transition metal carbonyls) to the most ionic type (transition metal fluorides).

Since the co-ordination theory of Werner and with the development of quantum mechanics, chemists' ideas of bonding have changed considerably. Three theories have been used to explain the structure, stability and general properties of these co-ordination compounds. The crystal field theory developed by Bethe takes into account only the electrostatic interaction between the metal ions and the surrounding ligands and thus this theory is largely limited to ionic complexes. The valence-bond theory developed by Pauling enjoyed initial successes especially in explaining magnetochemical properties of complexes but this theory is inadequate in explaining the spectral properties of complexes. Modified molecular-orbital theory when applied to transition metal complexes is known as Ligand field theory is at present the most suitable theory for explaining qualitatively and quantitatively (with the limitation inherent in all calculations which involve approximations) the observed properties of the complexes. A number of good books have appeared on this theory^{1, 2, 3}.

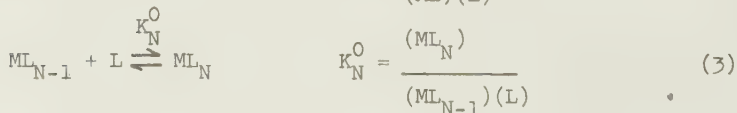
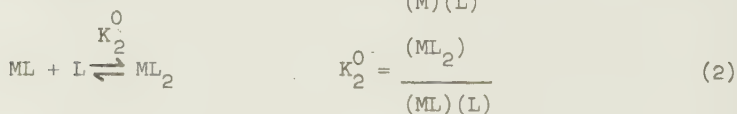
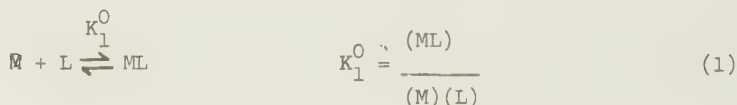
The study of complexes can either be carried out in the solid state or in solution. The study of complexes in the solid state furnish information such as bond lengths (X-ray diffraction, neutron

diffraction), bond strength (infra red, raman), structural determination (n.m.r, n.q.r, e.s.r) and nature of chemical bond (n.q.r, mössbauer, photoelectron spectroscopy).

In solution one studies either the kinetic properties of a complex i.e. it's rate of formation or dissociation or the thermodynamic property i.e. it's stability with respect to the corresponding aquocomplex.

The most important thermodynamic characteristic of a complex in solution is the equilibrium constant for the formation of the complex from the central metal ion and ligands in solution. It is characteristic of these complexes that they retain their identity to a large extent in solution although they may undergo partial dissociation.

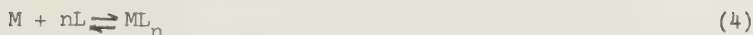
If we have a metal ion M and a monodentate ligand L in solution, then the activity $(ML_n)^*$ of a species ML_n is related to the activities M, L by the law of mass action.



Where N = maximum co-ordination number of the metal ion for the ligand L and $K_1^O, K_2^O \dots K_N^O$ are called the stepwise formation constants.

* Throughout this work concentrations of species will be denoted by square brackets and their activities by curved brackets.

For the overall reaction :



$$\beta_n^0 = \frac{(ML_n)}{(M)(L)^n} \quad (5)$$

Where β_n^0 = overall stability constant and is related to the stepwise stability constant by the following relation :

$$\beta_n^0 = K_1^0 K_2^0 \dots K_n^0 \quad (6)$$

The solvent has been omitted in the above equations although the metal ions are invariably solvated but the omission is justified provided that the reactants are in such low concentrations that the activity in water remains effectively constant.

Equilibrium constants consist of a unitary part characteristic of the reactants and of a cratic part which depends only on the number of interacting species. The cratic part for the above reaction at 25° if the solvent is water is 55⁻ⁿ, so that the unitary equilibrium constant is given by :

$$\log \beta_n^0 = \log \beta_n^0 + n \log 55.5 = \log \beta_n^0 + 1.74n \quad (7)$$

The concentration of ML_n is related to the concentrations of M, L and ML_{n-1} by the corresponding stoichiometric stability constants.

$$\beta_n = [ML_n] / [M][L]^n = \beta_n^0 / \prod \gamma_i^{\nu_i} \quad (8)$$

$$K_n = [ML_n] / [ML_{n-1}][L] = K_n^0 / \prod \gamma_i^{\nu_i} \quad (9)$$

Where ν_i are the stoichiometric coefficient of the participant species and γ_i are their activity coefficients on the appropriate concentration scales.

Experimental values of the activity coefficient are seldom available and for this reason stoichiometric stability constants are often determined in solution of constant ionic strength, where activity coefficients although unknown remain constant.

The stability constant is related to the free energy of formation by the well known relationship :

$$\Delta G = -RT \ln K \quad (10)$$

Abegg⁴ was the first to point out that complex formation is a stepwise process. Since the classic work on metal ammine formation by J. Bjerrum⁵, the rapid growth in interest in this field is shown by the number of books^{6 - 11} published on this subject and the compilation of the two volumes of data of constants by the Chemical Society^{12, 13}.

A large number of methods are now used for the determination of stability constants. These methods are given in detail in a number of books^{14, 15} and articles. I shall describe in detail only the methods that were used in this work and these are given in the next chapter under the experimental section.

Aim of this work

The stability constants of complexes in solution generally refer to the stability relative to aquocomplexes i.e. complexes with water as ligands. Hence in any such studies the metal aquo ions must be well characterised. The aqueous chemistry of the second and third row transition metal series are not in general well defined since in solution they generally occur as the oxo (RuO_4^{2-} , TeO_4^- , ReO_4^-) or the chloro (IrCl_6^{3-} , PtCl_4^{2-}) ions. This is one of the reasons why there have been so few data on the stabilities of complexes of these metals when compared with the innumerable constants known for the first row transition metal ions.

Until recently the method of preparation of tetraaquo palladium (II) ions in solutions were either tedious or they resulted in solutions which gave highly absorbing impurities because of the formation of hydroxo complexes due to the instability to hydrolysis of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ ion. The method of Sundaram and Sandell¹⁶ which involves the dissolution of palladium in a mixture of nitric acid and perchloric acid followed by evaporation of nitric acid belong to the former category while Livingstone's¹⁷ preparation giving hygroscopic $[\text{Pd}(\text{H}_2\text{O})_4](\text{ClO}_4)_2$ belong to the latter category.

L. Rasmussen and C.K. Jørgensen¹⁸ have indicated an easy way of obtaining tetraquo palladium (II) ion in solution. The starting product in their preparation was brickred palladium sulphate which they prepared as described by Kane¹⁹. When PdSO_4 is dissolved in 1M HClO_4 a yellow solution is obtained which gives a characteristic spectrum of the tetraaquo ion and the spectrum remains unchanged even after the removal of the sulphate ion by the addition of barium perchlorate.

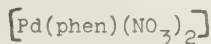
L. Rasmussen and C.K. Jørgensen¹⁸ have determined the formation constants of $[\text{Pd}(\text{NH}_3)_4]^{2+}$ and $[\text{Pd}(\text{en})_2]^{2+}$ spectrophotometrically and potentiometrically. Infact these have been the only complexes of palladium (II) ion together with the halo complexes for which the stability constants have been determined.

Livingstone ²⁰ has prepared complexes of the type $[\text{Pd}(\text{phen})\text{X}_2]$ where X = halide ions and $[\text{Pd}(\text{phen})\text{A}_2]^{2+}$ where A = NH_3 , en, py, glycinate ion. L. Rasmussen and C.K. Jørgensen ²¹ have studied the visible and near u.v. spectra of some of the above named complexes. The high affinity of one molecule of phenanthroline in these complexes is very striking. Because of this $[\text{Pd}(\text{phen})]^{2+}$ can be treated as a persistent entity. The aim of this work has been to determine the influence of the phenanthroline molecule in the complexes of the type $[\text{Pd}(\text{phen})\text{A}_2]^{2+}$ on the two residual positions.

CHAPTER II

EXPERIMENTAL

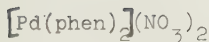
II (1) Preparations of compounds used in this work



To a solution of metallic palladium in concentrated nitric acid was added orthophenanthroline monohydrate in the ratio 1:1 and the resulting solution was diluted with distilled water while stirring, when a bright yellow precipitate was formed. The precipitate was filtered and washed with several portions of dilute nitric acid and ether. Alcohol was not used for the washing because it resulted in a partial reduction of Pd (II) to Pd metal. The precipitate was left in an oven to dry.

Microgravimetric analysis :

%	Pd	C	N	H
Found	25.83	35.23	13.82	2.28
Calc.	25.95	35.15	13.66	1.97

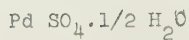


To a solution of Pd SO₄ in 1M HNO₃ was added a solution of phenanthroline in 0.1M HNO₃ in the ratio 1:2. The mixture was stirred well and left for half an hour when bright yellow crystals were formed leaving a colourless supernatant liquid. The crystals were filtered off, washed with dilute nitric acid followed by ether.

Microgravimetric analysis :

%	Pd	C	N	H
Found	18.1	49.05	14.21	2.74
Calc.	18.01	48.78	14.22	2.72

The corresponding paratoluenesulphonate salt was also prepared.



This was prepared as described by L. Rasmussen and C.K. Jørgensen¹⁸.

Microgravimetric analysis :

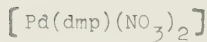
%	Pd	S	H
Found	50.2	15.9	0.28
Calc.	50.3	15.2	0.48

Pd(phen)Cl₂, Pd(phen)Br₂, Pd(phen)I₂, [Pd(phen)(NH₃)₂](ClO₄)₂, [Pd(phen)(NH₃)₂](NO₃)₂, [Pd(phen)(py)₂](ClO₄)₂, [Pd(phen)(py)₂](NO₃)₂, [Pd(phen)en](ClO₄)₂, [Pd(phen)en](NO₃)₂ were prepared as described by L. Rasmussen and C.K. Jørgensen²¹ except for the nitrates of the above mentioned complexes, for which instead of 1M NaClO₄, 1M or 2M potassium nitrate solutions were used.

Pd(phen)(OH)₂ and Pd en Cl₂ were kindly provided by prof. C.K. Jørgensen. From the microgravimetric analysis of the bright orange Pd(phen)(OH)₂ was found to be Pd(phen)(OH)₂.2H₂O

%	Pd	C	N	H
Found	30.	41.47	8.05	3.54
Calc.	29.8	40.4	7.8	3.96

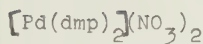
In the course of a few days, this material decomposes to a reddish orange wax, possibly due to polymerization via oxo bridges.



This was prepared in the same way as Pd(phen)(NO₃)₂. Instead of phenanthroline, -dimethylphenanthroline hydrate was used. Bright yellow crystal were obtained.

Microgravimetric analyses :

%	Pd	C	N	H
Found	24.38	38.45	12.7	2.82
Calc.	24.25	38.33	12.77	2.75



This was prepared in the same way as $[\text{Pd}(\text{phen})_2](\text{NO}_3)_2$. The pink precipitate obtained was found to be a mixture of mono and bis dimethylphenanthroline palladium (II) nitrate.

Microgravimetric analysis :

%	Pd	C	N	H
Found	22.0	43.3	8.06	3.18
Calc. for 1:2	16.45	51.98	12.99	3.74
Calc. for 1:1	24.25	38.33	12.77	2.75

$\text{Pd}(\text{dmp})\text{Cl}_2$, $\text{Pd}(\text{dmp})\text{Br}_2$ were prepared by following the same procedure as that described for the corresponding phenanthroline complexes. The dichlorodimethylphenanthroline palladium (II) was pale orange and the dibromodimethylphenanthroline palladium (II) brown and $\text{Pd}(\text{dmp})\text{I}_2$ was dark green.

Pale orange $\text{Pd}(\text{pic})\text{Cl}_2$ was also prepared in the same way using 2-methylaminopyridine. The corresponding nitrate complex could not be prepared because of the great solubility of these complexes.

Materials

Palladium metal - Metaux Precieux S.A.

K_2PdCl_4 H. Drijbhout and Zoon's Edel Metaal bedrijven

K_2PdBr_4

o-phenanthroline monohydrate Fluka puriss p.a.

Dimethylphenanthroline Fluka puriss p.a.

Ethylenediamine

Pyridine

Ammonia

HNO_3 , $HClO_4$ and H_2SO_4

Sodium perchlorate

Sodium nitrate

Potassium nitrate

Ammonium nitrate

Potassium chloride

Mohr's salt

Potassium bromide

All chemicals used were of reagent grade.

I(2) Experimental Procedure

Potentiometric Method

The experimental set up used for the study of complex formation potentiometrically is shown in fig. (I).

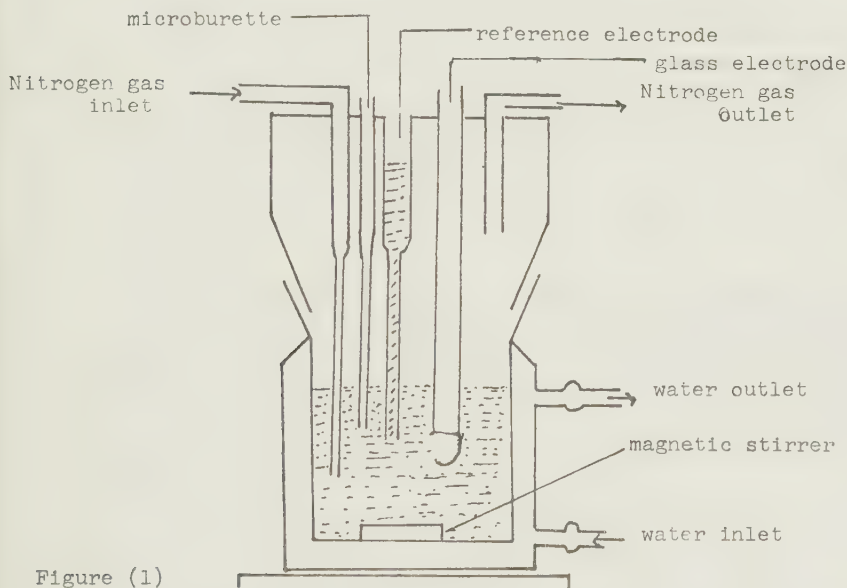


Figure (1)

The apparatus consisted of a double-walled glass container with outlets for water to be circulated for thermostating. The glass container was fitted with a multiholed cap through which glass electrode, reference electrode, incoming and outgoing nitrogen gas, microburette terminal could be introduced.

The pH was measured using Metrohm digital and non digital pH meters. The pH meter was initially calibrated using standard buffer solutions of pH 7 (Metrohm) and pH 4 (0.05M potassium-phthalate) although for calculations, the corresponding titration carried out in the absence of complexing agent was used as reference. The digital pH meter reading were ± 0.01 pH and the non digital ± 0.05 pH.

II(3) Preliminary experiments

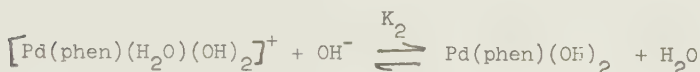
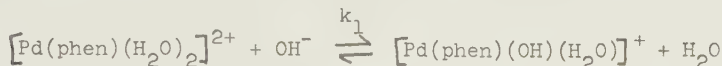
As discussed in the introductory section, stability constants are a function of activities but since activity coefficients are very rarely known or can be calculated only approximately and even that involves some questionable assumptions, the stability constant measurements are generally carried out at high ionic strengths. Although the activity coefficients at these ionic strength are unknown, they can be assumed to be constant. In choosing salts to keep the ionic strength constants, care must be taken to choose only the anions of salts that do not form complexes with the metal ions under study. Perchlorate ions have been found to be the most suitable for this purpose for they are known not to form complexes or only very weak complexes with most metals.

The monophenanthroline complexes of palladium with perchlorate anions were found to be extremely insoluble in water and common organic solvents. Hence, unfortunately the perchlorates of these complexes could not be used for the study of formation constants.

Several anions were tried in order to obtain a fairly soluble salt. Some of the anions tried were : naphthalene sulphonate, para-toluene sulphonate, fluoromethane sulphonate, fluoroborate, acetate ions. All these anions formed insoluble salts with the corresponding palladium complex. The only anion with sufficient solubility was the nitrate ion. The solubility of this ion was not high enough to allow determinations of stabilities to be carried out at constant ionic strength. Because of a lack of suitable anion, the stability constants were carried out with the nitrates bearing in mind the possibility of this ion forming weak nitrate complexes in solution.

II(4) Formation of hydroxo complexes

The formation constants for the formation of hydroxo complexes of monophenanthroline palladium (II) (see equations below) were studied both potentiometrically and by conductivity measurements.



Since $\text{Pd}(\text{phen})(\text{NO}_3)_2$ (to give the aquo ion $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ in acidic solution) and $\text{Pd}(\text{phen})(\text{OH})_2$ (giving $[\text{Pd}(\text{phen})(\text{OH})_3]^-$ in alkaline solution) were available as starting materials, the formation constants were measured in both directions i.e. starting from the aquo complex and going to the hydroxo complex and vice versa.

I(4)(a) Formation of the aquo complexes from the hydroxo complexes

$\text{Pd}(\text{phen})(\text{OH})_2$ was dissolved in 0.01M sodium hydroxide (carbondioxide free). 40 ml of this colourless solution (this volume was chosen because of the limited capacity of the thermo-stated container) was titrated with 0.1M HNO_3 under nitrogen atmosphere. The acid was added from a microburette ($\Delta V = \pm 0.005\text{ml}$). The solution was stirred continuously with a magnetic stirrer and the titration was carried out under nitrogen atmosphere to prevent carbondioxide from entering the system. The experimental set up is shown in figure (I). Acid-base titration in the absence of the complex was carried out under the same conditions. This procedure was repeated for different concentrations of the complex. The concentration range used was from 1×10^{-4} moles per litre to 1×10^{-3} moles per litre. The upper limit was necessitated by

the low solubility of the aquo complex (the solution up to 5m.Molar can be prepared with Pd(phen)(OH)_2) and the lower limit was imposed because of the imprecision in the measurements of the pH for at low concentrations of the complex the difference in pH between the measurements carried out in the absence and in the presence of complex becomes immeasurably small.

I(4)(b) The formation of hydroxo complexes from the aquo ion

In this case the starting material was the dinitrato-monophenanthroline palladium (II), $\text{Pd(phen)(NO}_3)_2$. This complex was dissolved in 0.01 M HNO_3 and the pale yellow solution was titrated with a solution of 0.1 M sodium hydroxide added from a microburette. The experimental procedure and set up were the same as described above. Titrations were also carried out in the absence of the complex. The concentration range of palladium used was $1 \times 10^{-4}\text{M}$, to $1 \times 10^{-3}\text{M}$ for the same reasons as mentioned above in the study of formation of aquo complexes from the hydroxo complexes.

I(4)(c) Conductivity Measurements

For measuring the conductivity of the solution, a platinum electrode of the type shown in fig. (II) was used. The cell constant for the electrode was found by making conductivity measurements in potassium chloride solutions, the conductivities of which are accurately known. The values of the conductivities for the potassium chloride solutions used are given in the calculation section and were taken from reference 22.

The cell constant was found to be 0.41 cm^{-1}

Wiss. techn. conductivity meter -LBR was used for conductivity measurements.

The conductometric titrations were carried out only for solutions starting from the hydroxo complexes. The purpose of these measurements was to find out if there was any trihydroxo monophenanthroline palladium (II) formed. The same experimental

set up and procedure as described for the potentiometric measurements was used. Instead of the pH electrodes, a platinum electrode was inserted. The conductivities of solution were determined both in the absence and in the presence of the complex.

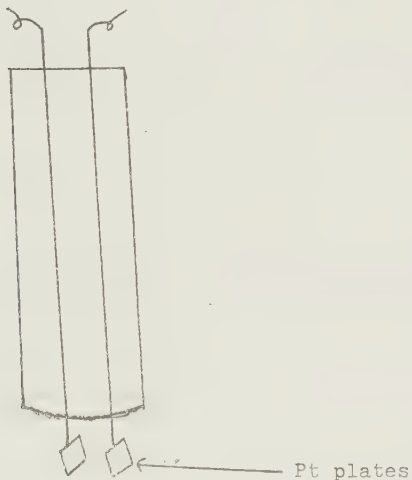


Figure (II)

II(5) Formation of ammine complexes

The formation of palladium diammine monophenanthroline was studied potentiometrically.

$\text{Pd(phen)(NO}_3)_2$ was dissolved in a solution of 0.01 M HNO_3 containing ammonium nitrate. This solution was titrated with a solution of 0.1 M sodium hydroxide using the experimental set-up shown in figure (I) and the pH of the solution measured. Titration in the absence of the complex but in solutions containing ammonium nitrate was carried out under the same experimental conditions. Titrations were carried out by varying both the total metal concentration and the total ammonium nitrate concentration.

In each case corresponding titrations in the absence of the complex was carried out. The concentration of the complex was varied from $1 \times 10^{-4}\text{M}$ to $7.5 \times 10^{-4}\text{M}$ and the ammonium nitrate concentration 10^{-2}M to $2 \times 10^{-2}\text{M}$. The dissociation constant of ammonium ion was determined independently.

Spectrophotometric measurements

The formation constants of $[\text{Pd(phen)(py)}_2]^{2+}$, $[\text{Pd(phen)en}]^{2+}$ and $[\text{Pd(phen)}_2]^{2+}$ could not be carried out potentiometrically because of the stabilities of these complexes which would require carrying out determinations in fairly acid solution, a region in which pH varies very slowly although the corresponding $[\text{H}^+]$ concentration is very high. Unicam SP 8000 recording spectrophotometer was used for most measurements and Beckmann D.B.G. used for the formation of $[\text{Pd(phen)}_2]^{2+}$ by the method of Job. The spectral changes took place near the u.v. range and hence the spectra were generally recorded between 450 - 300 nm range.

II(6) Formation of $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$

The spectrum of $[\text{Pd}(\text{phen})(\text{py})_2](\text{ClO}_4)_2$ in water was reported by L. Rasmussen and C.K. Jørgensen²¹. To a solution of $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$ in water different amounts of HNO_3 was added and the solutions were left to equilibrate in a thermostat at 25°C . Although the decomposition of $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$ to the corresponding aquo ion reached equilibrium in a few minutes nevertheless these solutions were left for a few hours to ensure complete reaction. The absorption spectra of these complexes were measured using 1 cm quartz cells. Absorption spectra were also measured for undecomposed $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$ and $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$.

Absorption spectra were also taken of solutions prepared by adding a known concentration of pyridine to a solution of $\text{Pd}(\text{phen})(\text{NO}_3)_2$ at known acid strengths. The spectrum of these solutions were in good agreement with those corresponding to the same equilibrium mixture prepared by acidifying $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$.

II(7) Formation of $[\text{Pd}(\text{phen})\text{en}]^{2+}$

The absorption spectrum of palladium (II) monoethylenediamine phenanthroline complex has previously been reported²¹. To a solution of $[\text{Pd}(\text{phen})\text{en}](\text{NO}_3)_2$ known amounts of HNO_3 was added and the solution left to equilibrate in a thermostat at 25°C for a few hours. The absorption spectrum of these solutions were recorded in the near ultraviolet region. In some case solutions were left overnight to see if the spectrum of these solutions corresponded to the spectrum of the same solutions taken a few hours after mixing.

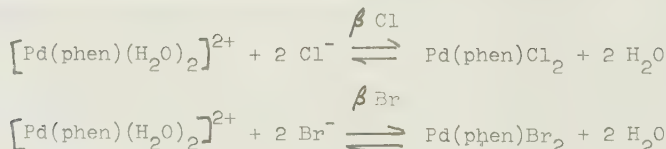
Absorption spectrum were also taken of solutions which were prepared by adding a known concentration of ethylenediamine to a solution of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$. An absorption spectrum of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ was also taken. The acid dissociation constants of ethylenediamine was measured potentiometrically.

II(8) Formation of $[\text{Pd}(\text{phen})_2]^{2+}$

To a solution of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ (prepared as usual by dissolving $\text{Pd}(\text{phen})(\text{NO}_3)_2$ in an acidic medium) different amounts of phenanthroline solutions (corresponding to a definite ratio of Pd/phen) were added at the same acid concentration and the solutions were left to equilibrate. Spectrum of these solutions were also measured at different pH. Because of the low solubilities of both $[\text{Pd}(\text{phen})_2](\text{NO}_3)_2$ and $\text{Pd}(\text{phen})\text{NO}_3$ at pH 2, only low concentrations of palladium could be used. Since the molar extinction coefficient of these complexes are not very high, 4 cm quartz cells were used for the study of these complexes.

The method of continuous variation (Job's method) was used to characterise the complex $[\text{Pd}(\text{phen})_2]^{2+}$. Solutions were prepared by mixing palladium diaquophenanthroline and phenanthroline in the ratio $x:y$ such that $x+y$ remained constant. The solutions were all made at pH 3 because at this pH no significant decomposition of the bis-complex takes place (by comparing the spectrum of $[\text{Pd}(\text{phen})_2](\text{NO}_3)_2$ in water and at pH 3) and also $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ is not much hydrolysed ($\text{pK} = 3.3$). The spectrum of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and phen. H^+ were measured at the same pH. The dissociation constant for the phenanthrolinium ion was determined potentiometrically.

II(9) Formation constants of chloro and bromo complexes of monophenanthroline palladium (II)



The formation constants for the above reactions were determined indirectly. Since the dihalophenanthroline palladium (II) complexes are insoluble in water, addition of potassium salts of the halide ions to a solution of bisphenanthroline palladium (II) results in the precipitation of the corresponding halo complex together with the release of one molecule of phenanthroline.



where X = halide ion

The amount of $\text{Pd}(\text{phen})\text{X}_2$ formed was determined by gravimetric analysis. The amount of phenanthroline formed in the reaction was determined spectrophotometrically by reacting it with a solution of ferrous sulphate and measuring the optical density of the resulting solution at 510 nm. The extinction coefficient of trisphenanthroline iron(II) under similar experimental conditions was found separately. To ensure that the addition of a solution of iron (II) to a solution containing $[\text{Pd}(\text{phen})_2]^{2+}$ did not result in the formation of trisphenanthroline iron (II), in the reaction of $[\text{Pd}(\text{phen})_2]^{2+}$ + halide ions, the halide ions were replaced by nitrate ions and the spectra of the solution in the presence of iron (II) were measured at 510 nm. The spectra did not show any absorption at this wavelength.

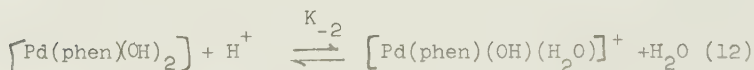
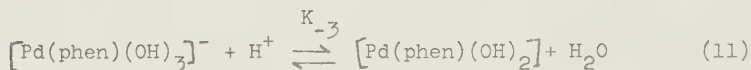
CHAPTER III

METHOD OF CALCULATION

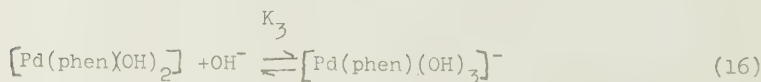
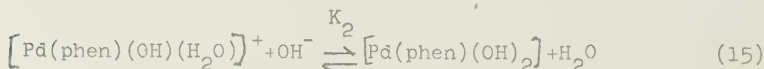
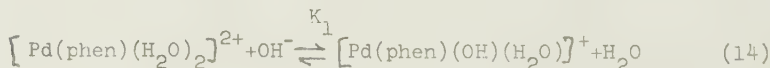
III(1)(a) Formation of diaquo phenanthroline palladium (II) from the corresponding hydroxo complex

In the presence of excess of hydroxide ions, dihydroxo monophenanthroline palladium (II) will mainly be in the form of trihydroxophenanthroline palladium (II) ion, $[\text{Pd}(\text{phen})(\text{OH})_3]^-$.

Addition of acid to the hydroxo complex would results in the following reactions :



where the reciprocal of K_{-3} , K_{-2} , K_{-1} are the hydrolysis constants of the corresponding aquo complexes. Since one is interested in the stability constants for the formation of the hydroxo complexes from the corresponding aquo complexes, the relationship between K_{-3} , K_{-2} and K_{-1} and K_1 , K_2 and K_3 can be obtained from the following reactions :



$$K_1 = K_{-1}/K_w$$

$$K_2 = K_{-2}/K_w$$

$$K_3 = K_{-3}/K_w$$

Where K_w is the ionic product of water and was taken to be 10^{-14} .
Total concentration of metal $T_{pd} = [C_0] + [C_1] + [C_2] + [C_3] =$ initial concentration of $Pd(phen)(OH)_2$, where :

$$C_0 = [Pd(phen)(H_2O)_2]^{2+}$$

$$C_1 = [Pd(phen)(OH)(H_2O)]^+$$

$$C_2 = [Pd(phen)(OH)_2]$$

$$C_3 = [Pd(phen)(OH)_3]^-$$

$$\text{Total concentration of hydroxide ion : } T_{OH} = C_{OH} + 2T_{pd} \quad (17)$$

where C_{OH} = initial concentration of sodium hydroxide

$2T_{pd}$ = since there are two hydroxide ion per palladium.

The last term in equation (17) appears since, the starting material for this study was the dihydroxophenanthroline palladium (II).

The formation number $\bar{n}$, defined as the average number of ligand, in this case the hydroxide ion, attached to the metal is :

$$\bar{n} = \frac{[C_1] + 2[C_2] + 3[C_3]}{T_{pd}} \quad (18)$$

$$= \frac{T_{OH} - [OH^-]}{T_{pd}} \quad (19)$$

where $[OH^-]$ = free hydroxide ion concentration.

Since the reaction was followed by measuring the pH of the solution

$$T_{OH} - [OH] = T_{OH} - T_H - \frac{K_w}{[H^+]} - \frac{K_w}{[OH^-]}$$

where T_H = total concentration of acid added

K_w = ionic product of water

$[H^+]$ = from the measured pH value = 10^{-pH}

The last term arises due to the hydrolysis of water

$$\bar{n} = \frac{T'_{OH} - T'_H - K_w/[H^+] - 10^{-14}/[OH^-]}{T'_{Pd}} \quad (20)$$

Since the volume of the total solution changes appreciably during the titration, the values of T_{OH} , C_H and T_{Pd} were corrected for the volume change.

$$T'_{OH} = \frac{V}{V+v} \times T_{OH}$$

$$T'_H = \frac{v}{V+v} \times T_H$$

$$T'_{Pd} = \frac{V}{V+v} \times T_{Pd}$$

where V = volume of the initial solution

v = volume of acid added

Only the stoichiometric concentrations were used in the calculations. No attempt was made to calculate the activity coefficients of the reacting species. The hydrogen ion concentration used was not evaluated directly from the measured pH values since the pH measurements generally refer to the activities of the hydrogen ions and not their concentrations. The hydrogen ion concentrations were evaluated by using the measured pH and comparing it with hydrogen ion concentration determined from the acid-base titration carried out in the absence of the complex, for the change in ionic strength were similar in both cases and change in ionic strength due to the presence of the complex was not very large.

The formation number $\bar{n}$ was plotted against $-pOH$ and the stability constants calculated by using the method of Bjerrum⁵. The values of pOH at $\bar{n} = 1/2, 3/2$ and $5/2$ were fairly well separated and thus did not necessitate solving three simultaneous equations of the form

$$\bar{n} + \beta_1[A](\bar{n}-1) + \beta_2[A]^2(\bar{n}-2) + \beta_3[A]^3(\bar{n}-3) = 0 \quad (21)$$

where $A = [OH^-]$

Simultaneous equations involving only two constants at a time were used to evaluate the stability constants from the formation curve i.e. the hydroxide concentration at $\bar{n} = 1/2$ and $\bar{n} = 3/2$ were substituted in the simultaneous equation given below

$$\left. \begin{aligned} \bar{n} = 1/2; \quad \bar{n} + \beta_1[OH^-]_{1/2}(\bar{n}-1) + \beta_2[OH^-]_{1/2}^2(\bar{n}-2) &= 0 \\ \bar{n} = 3/2; \quad \bar{n} + \beta_1[OH^-]_{3/2}(\bar{n}-1) + \beta_2[OH^-]_{3/2}^2(\bar{n}-2) &= 0 \end{aligned} \right\} \quad (22)$$

and the values found for β_1 and β_2 were improved by the iterative method. Similary values of $[OH^-]$ at $\bar{n} = 3/2$ and $5/2$ were used to solve the following simultaneous equation.

$$\left. \begin{aligned} \bar{n} = 3/2; \quad (\bar{n}-1) + K_2[OH^-]_{3/2}(\bar{n}-2) + K_2K_3(\bar{n}-3)[OH^-]_{3/2}^2 &= 0 \\ \bar{n} = 5/2; \quad (\bar{n}-1) + K_2[OH^-]_{5/2}(\bar{n}-2) + K_2K_3(\bar{n}-3)[OH^-]_{5/2}^2 &= 0 \end{aligned} \right\} \quad (23)$$

to obtained the values of K_2 and K_3 .

III(1)(b) The formation of hydroxo complex from diaquo-phenanthroline palladium (II)

The formation of the trihydroxophenanthroline palladium (II) was studied by titrating the aquo complex in acidic solution with 0.1 M sodium hydroxide.

In this case T_{Pd} = total palladium concentration
 = initial concentration of $[Pd(phen)(NO_3)_2]$
 T_{OH} = concentration of sodium hydroxide added
 T_H = initial concentration of nitric acid

The same procedure as that described in III(1)(a) was used for the calculation, except that instead of using equation (20) for the formation number $\bar{n}$, the following equation was used

$$\bar{n} = \frac{T'_{OH} - T'_H + [H^+] - K_w / [H^+]}{T'_{Pd}} \quad (24)$$

$$\text{where } T'_{OH} = \frac{V}{V+v} \cdot T_{OH}$$

$$T'_H = \frac{V}{V+v} \cdot T_H$$

$$T'_{Pd} = \frac{V}{V+v} \cdot T_{Pd}$$

The stability constants were evaluated as described in III(1)(a).

III(1)(c) Calculation from conductivity measurements

$$\text{Equivalent conductance } \Delta = \frac{K \times 1000}{C}$$

where K = specific conductance

C = concentration of solution in gram equivalent per litre

At infinite dilution $\Delta = l_+^0 + l_-^0$

where l_+^0 and l_-^0 are the ionic conductances of the cation and the anion respectively.

The specific conductance $K = \frac{\text{cell constant}}{R}$

where R is the resistance of the cell solution measured.

Using the known (previously determined) value of the cell constant, the specific conductance of the solution can be calculated. If the concentrations of the individual ions are known then the equivalent conductance of the solution can be calculated.

In the conductometric titration of dihydroxophenanthroline palladium (II) dissolved in known concentration of sodium hydroxide with nitric acid, the conductance of the initial solution will depend on whether or not the dihydroxo complex takes in a hydroxide ion to form the trihydroxophenanthroline palladium (II).

If the trihydroxo complex is formed, then the conductance of the solution will be given by :

$$\Delta = l_{\text{Pd(phen)(OH)}_3^-} + l_{\text{Na}^+} + l_{\text{OH}^-} \quad (25)$$

where $l_{\text{Pd(phen)(OH)}_3^-}$ = conductance of $[\text{Pd(phen)(OH)}_3]^-$ ion

l_{Na^+} = conductance of Na^+ from the initial concentration of sodium hydroxide

l_{OH^-} = conductance of free hydroxide ion present in solution
 = total concentration of hydroxide ion, T_{OH} (initial concentration of sodium hydroxide) - $C_{[\text{Pd(phen)(OH)}_3]^-}$
 (this is equal to the initial Pd(phen)(OH)_2 concentration, T_{Pd})

Since the conductance of monovalent ions are about the same, the specific conductance measured :

$$K_{\text{meas.}} = l \times \frac{T_{\text{Pd}}}{1000} + l_{\text{OH}^-} \times \frac{T_{\text{OH}^-} T_{\text{Pd}}}{1000} + l_{\text{Na}^+} \times T_{\text{OH}} \quad (26)$$

where l = conductance for a monovalent ion

l_{OH^-} = ionic conductance of hydroxide ion

l_{Na^+} = ionic conductance of $[\text{Na}^+]$ ion

If there is no trihydroxo complex formed then the ions present in solution are those due to the dissociation of the alkali i.e. Na^+ and hydroxide ion only since $\text{Pd}(\text{phen})(\text{OH})_2$ is a neutral molecule and hence non conducting.

Thus the conductivity of such a solution will be given by :

$$K_{\text{meas.}} = l_{\text{Na}^+} T_{\text{OH}} + l_{\text{OH}^-} T_{\text{OH}} \quad (27)$$

The difference in measured conductivities between the solution containing the complex and the one taken in the absence of the complex will be given by

$$(K_0 - K) \times 1000 = l_{\text{OH}} \times T_{\text{Pd}} - l \cdot T_{\text{Pd}}$$

where K_0 = specific conductance of the solution in the absence of the complex

K = specific conductance of the solution in the presence of the complex

A decrease in conductance on the addition of the complex is a certain indication of the formation of a trihydroxo phenanthroline-palladium (II) ion.

Since the ionic conductance of Na^+ and OH^- ions are well known, their values cited in the literature combined with an average value of conductance of a monovalent anion can be used to calculate the specific conductance of the solution containing the complex. This value can then be compared with the observed value.

During the titration, because of the volume change in the solution, the specific conductances have to be corrected for the effect of dilution and this is done by multiplying them by a factor of $\frac{V+v}{V}$ where V = initial volume of the solution and v = volume of acid added.

The conductance of the solution, before the neutralisation point, is given by :

$$K = l_{\text{mono}} \times \frac{[C_3]}{1000} + l_{\text{OH}} \times (T'_{\text{OH}} - [C_3]) + l_{\text{Na}} \times T'_{\text{OH}} + l_{\text{NO}_3} \times T'_{\text{H}} \quad (29)$$

where T'_{OH} and T'_{H} are the concentrations of hydroxide and acid respectively and C_3 = concentration of the trihydroxo complex.

The following values of conductances were used.

Values of equivalent conductance at 25°C²²

Ion	Δ
OH^-	198.5
H^+	349.8
NO_3^-	71.4
Na^+	50.1

Average value for a monovalent anion = 76

For the calibration of the electrode, potassium chloride solutions were prepared for which the following values of conductance were used :

$K = 0.012856$ for 0.1M KCl

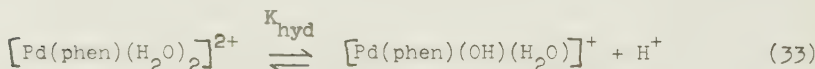
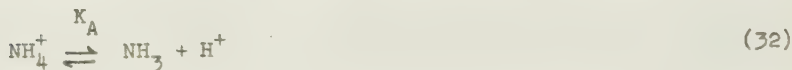
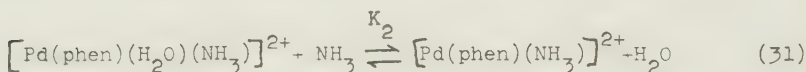
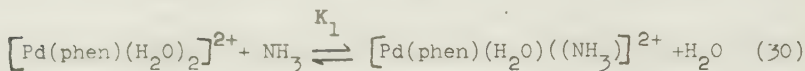
$K = 0.0014088$ for 0.01M KCl

The cell constant was found to be 0.411 cm^{-1}

III(2) Formation of diamminophenanthroline palladium (II) ion from the corresponding diaquophenanthroline palladium (II).

The formation of the ammine complexes were studied potentiometrically by titrating the aquo complex in acid solution containing ammonium nitrate with 0.1M sodium hydroxide solution.

The following equilibria are involved in the formation :



where K_1 and K_2 are the successive stability constants for the ammine formation, K_A = dissociation constant of the ammonium ion and K_{hyd} = hydrolysis constant for the aquo ion.

Total palladium concentration, T_{Pd} = initial concentration of $\text{Pd}(\text{phen})(\text{NO}_3)_2$

$$= [\text{C}_0] + [\text{C}_1] + [\text{C}_2] + [\text{C}_3] \quad (34)$$

where $[\text{C}_0]$ = concentration of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$
 $[\text{C}_1]$ = concentration of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})(\text{NH}_3)]^{2+}$
 $[\text{C}_2]$ = concentration of $[\text{Pd}(\text{phen})(\text{NH}_3)_2]^{2+}$
 $[\text{C}_3]$ = concentration of $[\text{Pd}(\text{phen})(\text{OH})(\text{H}_2\text{O})]^+$

Total concentration of ammonia produced, T_{NH_3} taking into account hydrolysis of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})]^{2+}$ i.e. equation (33)

$$T_{\text{NH}_3} = T'_{\text{OH}} - T'_H + [\text{H}^+] - K_w / [\text{H}^+] - \frac{K_{\text{hyd}}}{[\text{H}^+]} [\text{CO}] \quad (35)$$

where T'_{OH} = concentration of sodium hydroxide added

T'_H = concentration of nitric acid in the solution

$[\text{H}^+]$ = measured hydrogen ion concentration

= $10^{-\text{pH}}$

If the hydrolysis of the diaquo ion is neglected then equation (35) becomes :

$$T_{\text{NH}_3} = T'_{\text{OH}} - T'_H + [\text{H}^+] - K_w / [\text{H}^+] \quad (36)$$

free ligand concentration $[\text{NH}_3]$ is given by :

$$[\text{NH}_3] = \frac{K_A}{[\text{H}^+]} [T'_{\text{NH}_4} - T_{\text{NH}_3}]$$

where T'_{NH_4} = total ammonia concentration

= initial concentration of ammonium nitrate

$$[\text{NH}_3] = \frac{K_A}{[\text{H}^+]} \left[T'_{\text{NH}_4} - (T'_{\text{OH}} - T'_H + [\text{H}^+] - K_w / [\text{H}^+]) \right] \quad (37)$$

where $T'_{\text{OH}} = \frac{v}{V+v} \times T_{\text{OH}}$

$T'_H = \frac{V}{V+v} \times T_H$

where v = volume of sodium hydroxide added

V = initial volume of the solution

T_{OH} = initial concentration of sodium hydroxide added

T_H = initial concentration of nitric acid

$$\bar{n} = \frac{T_{\text{NH}_3} - [\text{NH}_3]}{T'_{\text{Pd}}}$$

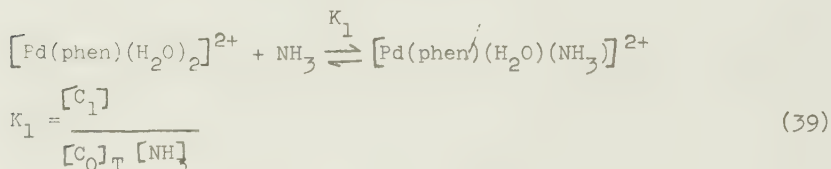
where $T'_{\text{Pd}} = \frac{V}{V+v} \times T_{\text{Pd}}$

$\bar{n}$, the formation number can be calculated from equations (36), (37) and (38) and the formation curve obtained by plotting $\bar{n}$ against pNH_3 .

It was found that $\bar{n}$ varied with the initial concentration of ammonium ions for the same concentration of the complex. This meant that the hydrolysis of diaquo phenanthroline palladium (II) ion took place at the same time as ammine formation and hence the hydrolysis of the diaquo had to be taken into account in the determination of the stability constants.

The $\bar{n}$ against pNH_3 curve obtained neglecting hydrolysis of the aquo ion, indicated that the two constants were not too close to each other thus making it possible to make the assumption that an approximate value of the first constant can be obtained by considering for $\bar{n} < 1$ only the formation of monoamminephenanthroline palladium (II) ion and ignoring the diammine formation.

For $\bar{n} < 1$



$$\begin{aligned} \text{where } T_{\text{Pd}} &= [\text{C}_0]_T + [\text{C}_1] \\ &= [\text{C}_0] + [\text{C}_b] + [\text{C}_1] \end{aligned}$$

$$\text{where } [\text{C}_0]_T = [\text{C}_0] + [\text{C}_b]$$

$$\bar{n} = \frac{[\text{C}_1]}{T'_{\text{Pd}}} = \frac{T_{\text{Pd}} - [\text{C}_0]_T}{T'_{\text{Pd}}} \quad (40)$$

$$\bar{n} = T'_{\text{OH}} - T'_{\text{H}} + [\text{H}^+]_{\text{th}} - \frac{K_w}{[\text{H}^+]_{\text{th}}} \quad (41)$$

$$\text{where } [H^+]_{th} = [H^+] - \frac{K_{hyd}}{[H^+] + K_{hyd}} [C_O] \quad (42)$$

where $[H^+] =$ measured hydrogen ion concentration

$\frac{K_{hyd}}{K_{hyd} + [H^+]} \cdot [C_O] =$ the hydrogen ion concentration arising from the hydrolysis reaction.

By putting $T'_{OH} - T'_H + [H^+] - K_W/[H^+] = A$

$$\frac{K_{hyd}}{[H^+] + K_{hyd}} = B$$

$$T_{NH_3} = A - B[C_O] \quad (43)$$

$$[NH_3] = \frac{K_A}{[H^+] - B[C_O]_T} [T'_{NH_4} - (A - B[C_O]_T)] \quad (44)$$

$$= \frac{K_A}{([H^+] - B[C_O]_T)} \cdot [T'_{NH_4} - A + B[C_O]_T] \quad (45)$$

$$\bar{n} = \frac{A - B[C_O]_T - \frac{K_A}{[H^+] - B[C_O]_T} [T'_{NH_4} - A + B[C_O]_T]}{T'_{Pd}} \quad (46)$$

equating (40) and (46) and rearranging, one gets

$$[C_O]_T^2 [B^2 - B] - [C_O]_T (B[H^+] + AB + BK_A - BT'_{Pd} - [H^+]) + (AH - K_A T_{NH_4} + AK_A - T_{Pd} [H^+]) = 0 \quad (47)$$

solving for $[C_O]$ by the standard method of solving quadratic equations, two solutions are obtained but one of them can be eliminated since it corresponds to a negative concentration.

Substituting for $[C_0]$ in equations (43) and (45), the total ammonia concentration and the free ammonia concentration can be calculated. $\bar{n}$ the formation curve can then be obtained from the following equation :

$$\bar{n} = \frac{T_{NH_3} - [NH_3]}{T'_{Pd}}$$

From a graph of $\bar{n}$ against pNH_3 , an approximate value of $\log K_1$ at $\bar{n} = 1/2$ can be obtained. The second complex can only be ignored upto a concentration of $\bar{n} = 0.7$.

By considering all the complexes present

$$\bar{n} = \frac{[C_1] + 2[C_2]}{T'_{Pd}} \quad (48)$$

$$T'_{Pd} = [C_0]_T + [C_1] + [C_2]$$

$$2T'_{Pd} = 2[C_0] + 2[C_1] + 2[C_2]$$

$$\begin{aligned} 2T_{Pd} - 2[C_0]_T &= 2[C_1] + 2[C_2] \\ &= [C_1] + 2[C_2] + K_1[NH_3][C_0] \end{aligned}$$

$$\bar{n} = \frac{2T_{Pd} - [C_0]_T [2 + K_1[NH_3]]}{T'_{Pd}} \quad (49)$$

equating (46) with (49) and rearranging one obtains

$$\begin{aligned} [C_0]_T^2 [B^2 - 2B + K_1 K_A B] - [C_0]_T [AB + B[H^+] + K_A B - 2B T'_{Pd}] \\ - K_1 K_A [T_{NH_4} - A] + AH - K_A T_{NH_4} + AK_A - T'_{Pd} [H^+] = 0 \end{aligned} \quad (50)$$

Solving the quadratic equation by using the approximate value of K_1 , $[C_0]$ can be evaluated by choosing the only concentration which has any physical meaning. By substituting for $[C_0]_T$ in equations (43) and (45) $\bar{n}$ and $[NH_3]$ can be found.

From the formation curve of $\bar{n}$ against $p\text{NH}_3$, taking the values of $p\text{NH}_3$ at $\bar{n} = 1/2$ and $3/2$, and solving the simultaneous equation obtained by rearrangement of the following equation

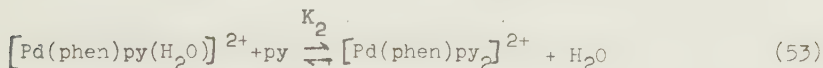
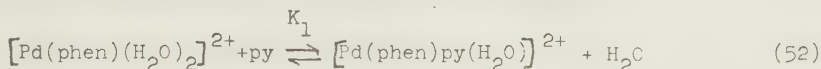
$$\bar{n} = \frac{K_1[\text{NH}_3] + 2K_1K_2[\text{NH}_3]^2}{1 + K_1[\text{NH}_3] + K_1K_2[\text{NH}_3]^2}$$

$$\bar{n} + K_1(\bar{n}-1)[\text{NH}_3] + K_1K_2(\bar{n}-2)[\text{NH}_3]^2 = 0 \quad (51)$$

the values of K_1 and K_2 can be computed by successive approximations.

Spectrophotometric method

I) (3) Formation constants for the formation of dipyridine phenanthroline palladium (II) from the corresponding aquo complex.



Although the absorption maximum of the complexes of diaquophenanthroline palladium (II) ion and dipyridinephenanthroline palladium (II) ion in the near ultra violet region lie at the same wavelength i.e. at $\lambda = 350$ nm, the extinction coefficients of the two complexes are sufficiently different to enable the use of the spectrophotometric method for the study of the formation of the pyridine complexes.

Since pyridine either as a neutral molecule or in the protonated form as the pyridinium ion does not absorb at this wavelength, the optical density D measured is related to the concentration of the complexes by the following relationship :

$$\frac{D}{l} = \epsilon_0[\text{C}_0] + \epsilon_1[\text{C}_1] + \epsilon_2[\text{C}_2] \quad (54)$$

where ϵ_0 = molar extinction coefficient of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ ion
 ϵ_1 = molar extinction coefficient of $[\text{Pd}(\text{phen})\text{py}(\text{H}_2\text{O})]^{2+}$ ion
 ϵ_2 = molar extinction coefficient of $[\text{Pd}(\text{phen})\text{py}_2]^{2+}$ ion

and $[C_0]$, $[C_1]$ and $[C_2]$ are the respective concentrations.

Since the values of ϵ_0 and ϵ_2 are known from the spectral measurements of the diaquophenanthroline palladium (II) and dipyridine-phenanthroline palladium (II) carried out separately, ϵ_1 can be calculated by applying Tsuchida's rule of average environment. Hence a theoretical plot can be made of $\bar{n}$ as a function of $\bar{\epsilon}$.

$$T_{Pd} = [C_0] + [C_1] + [C_2]$$

$$\bar{n} = \frac{[C_1] + 2[C_2]}{T_{Pd}} \quad (55)$$

From the optical densities measured of solutions containing known initial concentration of the diaquo ion and pyridine at a certain pH, the mean molar extinction coefficients can be calculated.

$$D = \frac{D}{l \times T_{Pd}} \quad (56)$$

where $\bar{\epsilon}$ = mean molar extinction coefficient

l = path length = 1 cm

T_{Pd} = total palladium concentration

= initial concentration of $[Pd(phen)(H_2O)_2]^{2+}$

From the calculated $\bar{\epsilon}$, the corresponding $\bar{n}$ can be obtained from the calibration graph of $\bar{n}$ against $\bar{\epsilon}$.

$$\bar{n} = \frac{T_H - [H^+]}{T_{Pd}} \quad (57)$$

where T_H = initial concentration of nitric acid.

Since at low pH $T_H \approx [H^+]$, the free hydrogen ion concentration is calculated instead of measuring it potentiometrically from equation (57) using the known values of $\bar{n}$, T_H and T_{Pd} .

Since the total pyridine concentration T_{py} is known, the free pyridine concentration can be calculated as described below.

$$\begin{aligned}
 T_{py} &= [pyH^+] + [py] + \bar{n}T_{Pd} \\
 [py] + [pyH^+] &= T_{py} - \bar{n}T_{Pd} \\
 [py] &= \frac{K_{py}[T_{py} - \bar{n}T_{Pd}]}{[H^+ + K_{py}]} \quad (58)
 \end{aligned}$$

where K_{py} = dissociation constant of the pyridinium ion.

The formation function is obtained by plotting $\bar{n}$ against $-\log[py]$. From the values of $\bar{n}$ at $\bar{n} = 1/2$ and $3/2$ the corresponding values of ppy are taken and the formation constants K_1 , K_2 calculated by the method of successive approximation by solving the simultaneous equation (59) of the form :

$$\bar{n} + K_1(\bar{n}-1)[A] + K_1K_2(\bar{n}-2)[A]^2 = 0 \quad \left\{ \begin{array}{l} \text{for } \bar{n} = 1/2 \\ \text{and} \\ \text{for } \bar{n} = 3/2 \end{array} \right\} \quad (59)$$

Formation constants calculation starting from $[Pd(phen)py]^{2+}$ ion.

Different amounts of acid was added to $[Pd(phen)py]^{2+}$ and the spectra of the resulting solution measured. From the measured optical densities, the mean molar extinction coefficients were calculated using equation (56). The corresponding $\bar{n}$ were obtained from the calibration graph of $\bar{n}$ against $\bar{\epsilon}$.

$\bar{n}$, the formation number is given by :

$$\bar{n} = 2 - \frac{T_H - [H^+]}{T_{Pd}} \quad (60)$$

where T_H = initial concentration of nitric acid

T_{Pd} = initial concentration of $[Pd(phen)(py)_2]^{2+}$

Since $\bar{n}$, T_H and T_{Pd} are known, the free hydrogen ion concentration can be calculated from equation (60). Total pyridine formed in the reaction $T_{py} = (2-\bar{n})T_{Pd}$

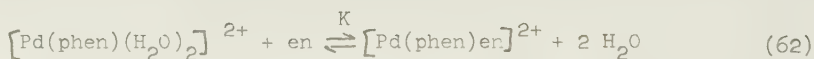
$$= [pyH^+] + [py]$$

The free pyridine concentration is given by :

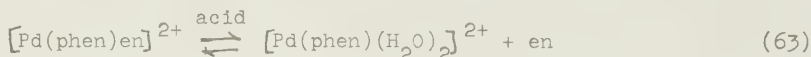
$$[py] = \frac{K_{py} T_{py}}{[H^+] + K_{py}} \quad (61)$$

From the formation curve, K_1 and K_2 were obtained as described in section III(3) .

III(4) The formation constant for the formation of monoethylenediamine-monophenanthroline palladium (II), $[Pd(phen)en]^{2+}$



The formation constant for the above reaction was studied both by the formation of $[Pd(phen)en]^{2+}$ by mixing ethylenediamine and $[Pd(phen)(H_2O)_2]^{2+}$ at different pH and also by the decomposition of $[Pd(phen)en]^{2+}$ by the addition of different amounts of acid.



The absorption maximum of both $[Pd(phen)en]^{2+}$ and $[Pd(phen)(H_2O)_2]^{2+}$ lie at $\lambda = 350$ nm but their extinction coefficient are different thus making spectrophotometric method for the study of these complex possible.

Calculation for measurements using reaction (63).

The mean molar extinction coefficient $\bar{\epsilon}$ is given by :

$$\bar{\epsilon} = \epsilon_0 [C_0] + \epsilon_1 [C_1] \quad (64)$$

where $\bar{\epsilon} = \frac{D}{l T_{Pd}}$

where D = measured optical density

l = path length = 1 cm

T_{Pd} = total palladium concentration

= initial concentration of $[Pd(phen)en]^{2+}$

$[C_0]$ = concentration of $[Pd(phen)(H_2O)_2]^{2+}$

ϵ_0 = molar extinction coefficient of $[Pd(phen)(H_2O)_2]^{2+}$

$[C_1]$ = concentration of $[Pd(phen)en]^{2+}$

ϵ_1 = molar extinction coefficient of $[Pd(phen)en]^{2+}$

From the known values of ϵ_0 , ϵ_1 and $\bar{\epsilon}$, the concentrations $[C_0]$ and $[C_1]$ can be calculated.

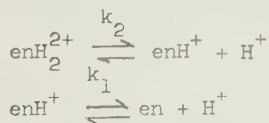
$$[C_1] = T_{Pd} \frac{(\bar{\epsilon} - \epsilon_1)}{(\epsilon_0 - \epsilon_1)} \quad (65)$$

$$[C_0] = T_{Pd} - [C_1] \quad (66)$$

The total ethylenediamine concentration produced in the reaction T_{en} , is given by :

$$T_{en} = [C_0] = [en] + [enH^+] + [enH_2^{2+}] \quad (67)$$

The free ethylenediamine concentration $[en]$, can be calculated from the total ethylenediamine concentration and the acid dissociation constants of ethylenediamine.



$$[en] = \frac{[C_0] \cdot k_1 k_2}{k_1 k_2 + k_2 [H^+] + [H^+]^2} \quad (68)$$

Since the acid concentration T_H used were high, the free hydrogen ion concentration $[H^+]$ was taken to be the same as T_H since $T_H \approx [H^+]$.

$$\bar{n} = \frac{[C_1]}{T_{Pd}} \quad (69)$$

Knowing $\bar{n}$ and $[en]$, the formation constant K for the formation of $[Pd(phen)en]^{2+}$ can be calculated from the formation curve.

From spectral measurements taken of reaction (62), the optical densities were measured for solutions made by mixing $[Pd(phen)(H_2O)_2]^{2+}$ in nitric acid with ethylenediamine. From the measured optical densities, the concentrations of $[Pd(phen)(H_2O)_2]^{2+}$ and $[Pd(phen)en]^{2+}$ were calculated using equations (66) and (65) and using the initial concentration of $[Pd(phen)(H_2O)_2]^{2+}$ for T_{Pd} .

The total ethylenediamine concentration in this case is the initial concentration of ethylenediamine used.

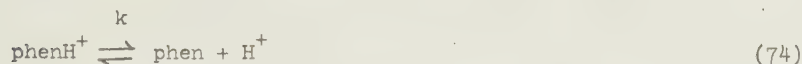
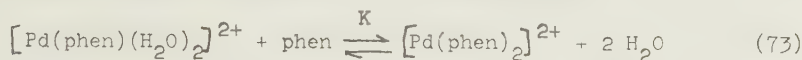
$$T_{en} = [en] + [enH^+] + [enH_2^{2+}] + [C_1] \quad (70)$$

$$T_{en} - [C_1] = [en] + [enH^+] + [enH_2^{2+}] \quad (71)$$

$$[en] = \frac{(T_{en} - [C_1]) \cdot k_1 k_2}{k_1 k_2 + k_2 [H^+] + [H^+]^2} \quad (72)$$

The total acid concentration T_H was used for $[H^+]$. The formation constant was found from the formation curve.

- (5) The formation of bisphenanthroline palladium (II) $[\text{Pd}(\text{phen})_2]^{2+}$
from diaquomonophenanthroline palladium (II) ion.



$[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$, $[\text{phenH}^+]$ and $[\text{Pd}(\text{phen})_2]^{2+}$ all three absorb in the near u.v. region of the spectra. The measured optical density is related to the concentration of the different species present in the solution in the following way.

$$\frac{D}{l} = \epsilon_0 [\text{C}_0] + \epsilon_1 [\text{C}_1] + \epsilon_{\text{phen}} C_{\text{phen}} \quad (75)$$

Where ϵ_0 and $[\text{C}_0]$ are the molar extinction coefficient and concentration of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ ion respectively, ϵ_1 and $[\text{C}_1]$ are the molar extinction coefficient and concentration of $[\text{Pd}(\text{phen})_2]^{2+}$ ion respectively, and ϵ_{phen} and C_{phen} are the molar extinction coefficient and concentration of phenanthroline ion $[\text{phenH}^+]$, respectively.

The path length, l of 4 cm was used.

For the calculation from optical densities, only the concentration of phenanthroline ion and not the total uncombined ligand concentration was considered because in the pH conditions used, the free concentration of phenanthroline is not high enough to contribute to the absorption measured.

$$\begin{aligned} \text{Total phenanthroline concentration } T_{\text{phen}} &= [\text{phen}] + C_{\text{phen}} + [\text{C}_1] \\ &\approx C_{\text{phen}} + [\text{C}_1] \end{aligned}$$

$$\text{Total palladium concentration } T_{\text{Pd}} = [\text{C}_0] + [\text{C}_1]$$

$$\begin{aligned} \frac{D}{4} &= \epsilon_0 [\text{C}_0] + \epsilon_1 (T_{\text{Pd}} - [\text{C}_0]) + \epsilon_{\text{phen}} (T_{\text{phen}} - [\text{C}_1]) \\ &= [\text{C}_0] (\epsilon_0 - \epsilon_1) + \epsilon_1 T_{\text{Pd}} + \epsilon_{\text{phen}} (T_{\text{phen}} - T_{\text{Pd}} + [\text{C}_0]) \end{aligned}$$

$$[C_0] = \frac{\frac{D}{4} - \epsilon_{\text{phen}} T_{\text{phen}} + \epsilon_{\text{phen}} T_{\text{Pd}} - \epsilon_1 T_{\text{Pd}}}{\epsilon_0 + \epsilon_{\text{phen}} - \epsilon_1} \quad (76)$$

$$[C_1] = T_{\text{Pd}} - [C_0] \quad (77)$$

$$\bar{n} = \frac{[C_1]}{T_{\text{Pd}}} \quad (78)$$

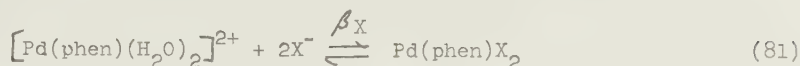
From equations (76), (77) and (74) the free phenanthroline concentration can be obtained

$$[\text{phen}] = \frac{(T_{\text{phen}} - [C_1]) k_{\text{phen}}}{[H^+] + k_{\text{phen}}} \quad (79)$$

From the experimentally determined optical densities, the concentration of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$, $[\text{Pd}(\text{phen})_2]^{2+}$ and $[\text{phen}]$ can be calculated from equations (76), (77) and (79). K can be found from the fundamental equation (73) defining stability constant or from the formation curve of $\bar{n}$ against $-\log \text{phen}$.

$$K = \frac{[\text{Pd}(\text{phen})_2]^{2+}}{[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+} [\text{phen}]} \quad (80)$$

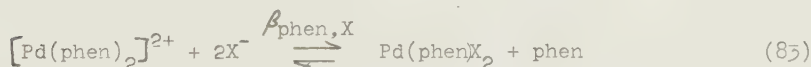
III(6) Formation constants for the formation of Pd(phen)X_2
 where $\text{X} = \text{Cl}^-$, and Br^- from $[\text{Pd(phen)(H}_2\text{O)}_2]^{2+}$



$$\beta_{\text{X}} = \frac{[\text{Pd(phen)X}_2]}{[\text{Pd(phen)(H}_2\text{O)}_2]^{2+} [\text{X}^-]^2} \quad (82)$$

The formation constant for the above reaction was not determined directly but by studying the formation of the dihalophenanthroline palladium (II) complex from the bisphenanthroline palladium (II) and then using the known formation constant of the bis complex β_{X} was calculated.

The following reaction was studied



$$\beta_{\text{phen,X}} = \frac{[\text{Pd(phen)X}_2][\text{phen}]}{[\text{Pd(phen)}_2]^{2+} [\text{X}^-]^2} \quad (84)$$

The results obtained from gravimetric analysis and spectrophotometric analysis were treated independently.

Gravimetric analysis

Addition of halide ions to $[\text{Pd(phen)}_2]^{2+}$ results in the precipitation of Pd(phen)X_2 . From the weight of Pd(phen)X_2 measured, the concentration of Pd(phen)X_2 can be calculated. From equation (83), it is obvious that the amount of Pd(phen)X_2 produced is equal to the amount of phenanthroline formed.

If the amount of Pd(phen)_2 formed = x mole/litre

T_{Pd} = total palladium concentration

= initial concentration of $[\text{Pd(phen)}_2]^{2+}$

T_{KX} = total halide concentration

= initial concentration of potassium salt of the halide ion

the equilibrium concentration of $[\text{Pd(phen)}_2]^{2+} = T_{\text{Pd}} - x$

the equilibrium concentration of $[\text{X}^-] = T_{\text{KX}} - 2x$

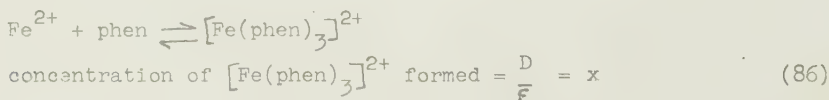
free phenanthroline concentration = $\frac{[\text{phen}]}{x \times k_{\text{phen}}}$
 $= \frac{[\text{H}^+] + k_{\text{phen}}}{[\text{H}^+] + k_{\text{phen}}}$

$$\beta_{\text{phen,X}} = \frac{x[\text{phen}]}{[T_{\text{Pd}} - x][T_{\text{KX}} - (2x)^2]} = \frac{x^2}{[T_{\text{Pd}} - x][T_{\text{KX}} - 2x^2]} \times \frac{k_{\text{phen}}}{[\text{H}^+] + k_{\text{phen}}} \quad (85)$$

where k_{phen} = dissociation constant of the phenH^+ ion.

Spectrophotometric analysis

The phenanthroline formed in reaction (83) was reacted with a solution of Mohr's salt and the optical density of $[\text{Fe(phen)}_3]^{2+}$ formed measured.



where D = optical density of solution measured

ϵ = molar extinction coefficient of $[\text{Fe(phen)}_3]^{2+}$ complex
 (determined under similar experimental conditions).

amount of phenanthroline formed = $3x$

amount of $\text{Pd}(\text{phen})\text{X}_2$ formed = amount of phenanthroline formed
= $3x$

$$\beta_{\text{phen},X} = \frac{(3x)^2}{(\text{T}_{\text{Pd}} - 3x)(\text{T}_{\text{KX}} - 6x)^2} \times \frac{k_{\text{phen}}}{[\text{H}^+] + k_{\text{phen}}} \quad (87)$$

where T_{Pd} and T_{KX} are the total initial concentrations of $[\text{Pd}(\text{phen})_2]^{2+}$ and KX respectively.

Calculation of β_X

Since K for the following reaction has already been determined



the formation constant β_X , for the formation of dihalophenanthroline palladium (II) from the diaquophenanthroline palladium (II) is related to K and $\beta_{\text{phen},X}$ by the following relationship

$$\beta_X = \frac{[\text{Pd}(\text{phen})\text{X}_2]}{[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+} [\text{X}^-]^2} = K \times \beta_{\text{phen},X} \quad (88)$$

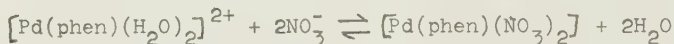
Knowing K and $\beta_{\text{phen},X}$, β_X can be calculated.

CHAPTER IV

RESULTS AND DISCUSSION

IV(1) Formation of nitrate complexes of palladium (II)

The formation constants for the following reaction :



have not been measured because of the difficulty in characterising this complex in aqueous solution. The conductivity measurements carried out on solutions of dinitrate monophenanthroline palladium (II) showed that the nitrate complex is completely dissociated in water. In fact the conductivity in water was found to be higher than calculated on the basis of complete dissociation because of the partial hydrolysis of the diaquomonomophenanthroline palladium (II) formed in solution.

Since nitrate complexes are generally weak any determination of the stability of these complexes would require a large excess of nitrate ion present in solution, a condition which could not be met in practice because of the low solubility of $[\text{Pd}(\text{phen})(\text{NO}_3)_2]$ both in water and in common organic solvents such as methanol, ethanol, dioxane, dichloromethane, etc.

Infra red measurements show that the nitrate ion in $[\text{Pd}(\text{phen})(\text{NO}_3)_2]$ is co-ordinated to the metal. Co-ordinated nitrates generally show strong absorption bands in the regions $1530-1480\text{cm}^{-1}$ and $1290-1250\text{cm}^{-1}$. In addition the vibration ν_1 , theoretically inactive for NO_3^- occurs as a strong peak in the nitrate complexes within the range $1034-970\text{cm}^{-1}$. Table (II) gives the i.r. bands for $[\text{Pd}(\text{phen})(\text{NO}_3)_2]$ together with that of $[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$, $[\text{Pd}(\text{dip})(\text{NO}_3)_2]$ and $[\text{Pd}(\text{dmp})(\text{NO}_3)_2]$ obtained by other workers.

TABLE II

Complex	ν_1 NO str.	ν_2 non planar deformation	ν_3 sym. NO ₂ str.	ν_4 asym. NO ₂ str.
$[\text{Pd}(\text{phen})(\text{NO}_3)_2]$	983 s	795 m	1275 vs 1265 vs 1250 vs	1500 vs 1492 vs 1467 vs
$[\text{Pd}(\text{dmp})(\text{NO}_3)_2]$	982 s	800 m	1285 vs 1270 s 1250 vs	1506 s 1487 s
$[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2](23)$	988	784 s	1274	1502 s
$[\text{Pd}(\text{dip})(\text{NO}_3)_2](23)$	989 s 979 s	975 s 801 s	1292 1274 1250	1517 1502

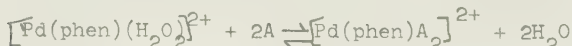
From Table (II) it can be seen that that nitrate ion in all the complexes cited act as ligand. The frequency of the absorption band , indicates the degree of covalent character of the metal-nitrate bond. No positive conclusion can be made about the bond strength if it is equated to the degree of covalency except to say that the nitrate ion is bound to more or less the same extent in all these complexes. The nitrate ion is most probably co-ordinated via only one of it's oxygen atom i.e. it is a unidentate ligand, since both $[\text{Pd}(\text{phen})(\text{NO}_3)_2]$ and $[\text{Pd}(\text{dmp})(\text{NO}_3)_2]$ prepared did not contain any H_2O molecule. E.S.C.A. measurements were made on $[\text{Pd}(\text{phen})(\text{NO}_3)_2]$, $[\text{Pd}(\text{phen})_2](\text{NO}_3)_2$ and $[\text{Pd}(\text{dmp})(\text{NO}_3)_2]$. The results given in Table III show that the N1s signal for NO_3^- for $[\text{Pd}(\text{phen})(\text{NO}_3)_2]$ and $[\text{Pd}(\text{dmp})(\text{NO}_3)_2]$ are very close to each other indicating a similarity in the bonding of NO_3^- in both these complexes whereas $[\text{Pd}(\text{phen})_2](\text{NO}_3)_2$ has a distinctly different N1s value.

TABLE III

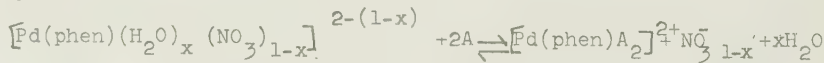
Complex	Nls (e.V.) (due to N of NO_3^-)	Nls (e.V.) (due to N of phen)
$[\text{Pd}(\text{phen})(\text{NO}_3)_2]$	411.76	405.25
$[\text{Pd}(\text{phen})_2](\text{NO}_3)_2$	411.1	405.5
$[\text{Pd}(\text{dmp})(\text{NO}_3)_2]$	411.75	405.2

The reason for the above discussion is to point out the fact that unlike most metal ions where the nitrate complexes can be considered as to be too weak to interfere in the determination of complex formation, in the case of Palladium (II) complexes, this is not so. Although the nitrate complex will not be very strong ($\log K \approx 1$) the so called diaquomonophenanthroline Palladium (II) might perhaps be partially in the form of the nitrate complex. Since all the measurements of stability constants have been made in solution containing nitrate ions, the constants obtained would be lower than the real constants by a factor depending on the constant of formation of the nitrate complex.

The constants obtained instead of referring to



probably refer to



IV(2) The formation of hydroxo complexes of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ ion.

Figures (1,2) gives a series of curves obtained for the titration of diaquomonophenanthroline palladium (II) ion with sodium hydroxide. The corresponding formation curve is shown in fig. (3). It can be seen that $\bar{n}$, the formation number does not depend on the concentration of metal used indicating that there in the concentration range studied there is little formation of polynuclear complexes.

Figure 1

- 47 -

Titration curves of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ in 0.01M HNO_3 with 0.1M NaOH .

1... Concentration of complex (1): $2.4932 \times 10^{-4}\text{M}$; (2): $3.7528 \times 10^{-4}\text{M}$;
(3): $1.5057 \times 10^{-4}\text{M}$

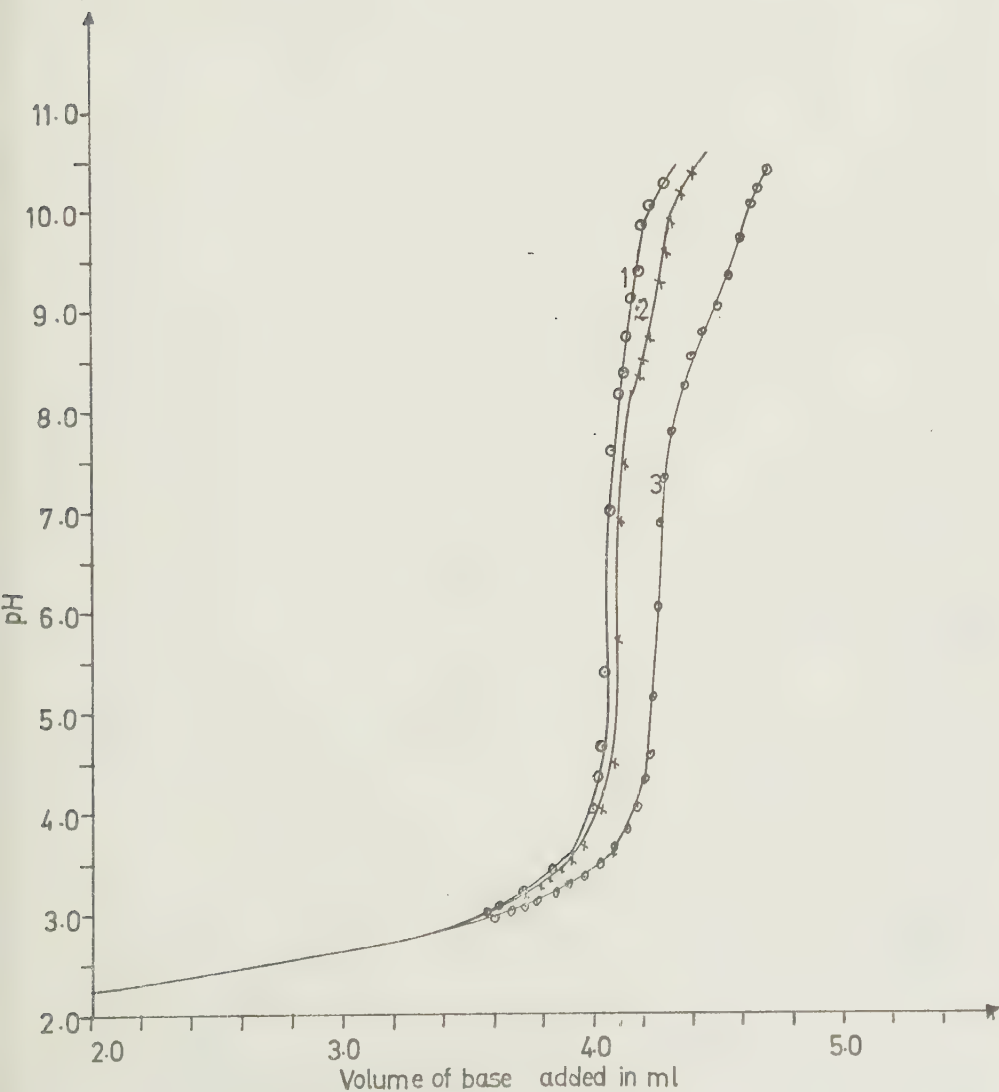


Figure 2

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Titration curves of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ ($C_{\text{Pd}} = 2.4932 \times 10^{-4} \text{ M}$) in 0.01 M HNO_3 with 0.1 M NaOH .

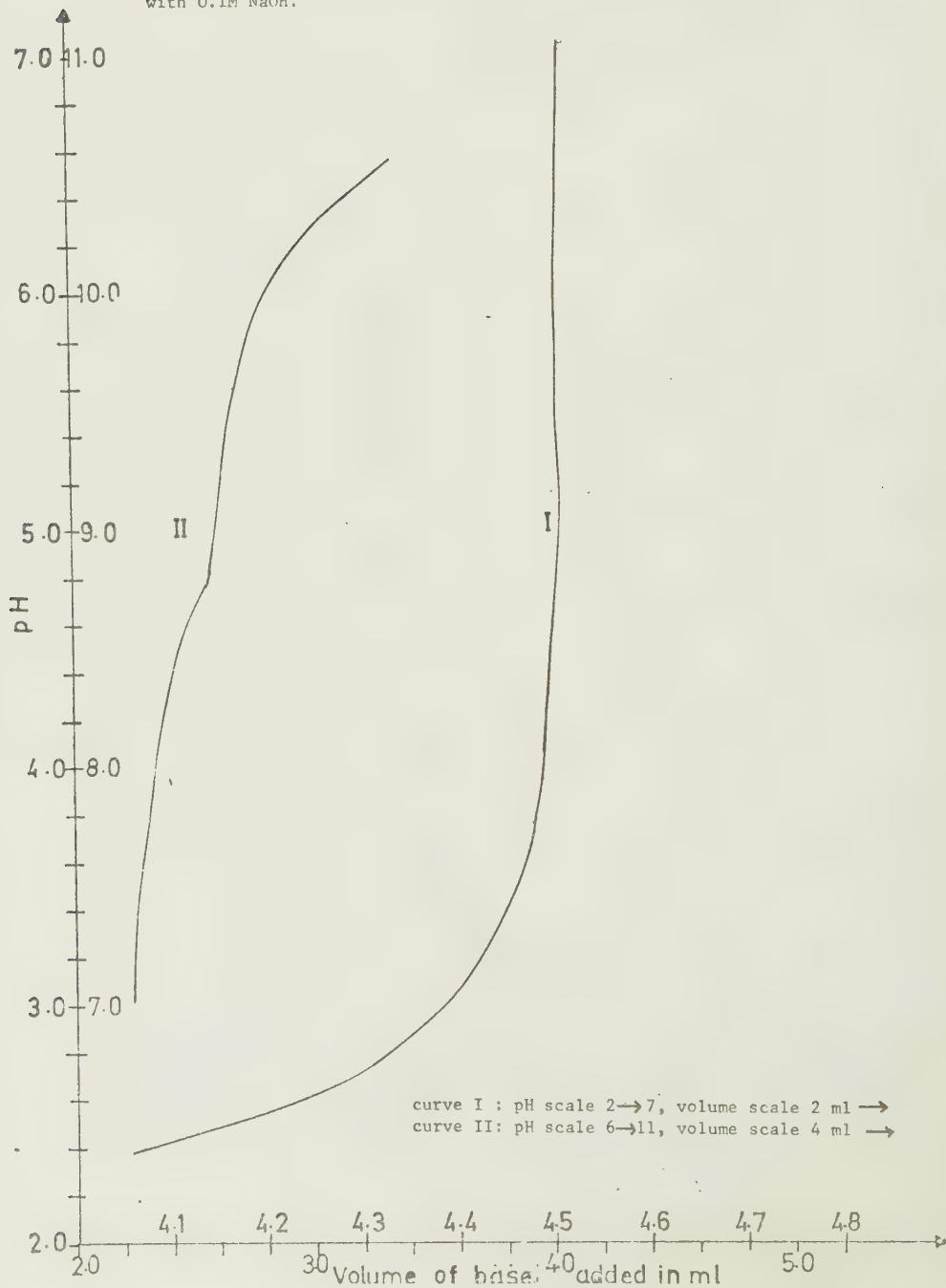


Figure 3

Formation curve for the hydroxocomplexes of $[\text{Pd}(\text{phen})]^{2+}$.

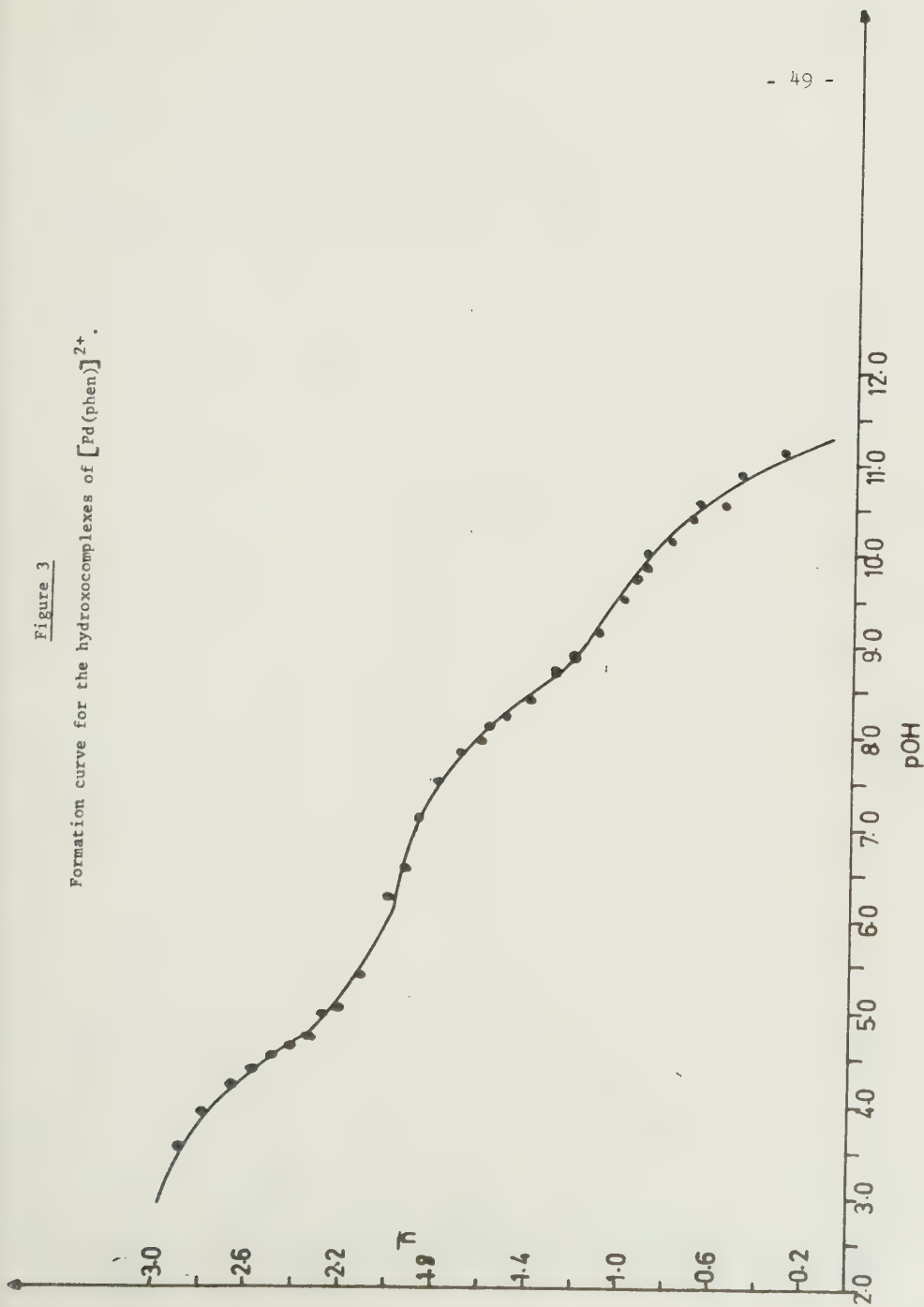


Figure 4

Titration curves of $[\text{Pd}(\text{phen})(\text{OH})_2]$ in 0.01M NaOH with 0. 1M HNO_3 .

$\times$: $1.012 \times 10^{-3}\text{M}$ $[\text{Pd}(\text{phen})(\text{OH})_2]$; $\bullet$: $5.0664 \times 10^{-4}\text{M}$ $[\text{Pd}(\text{phen})(\text{OH})_2]$

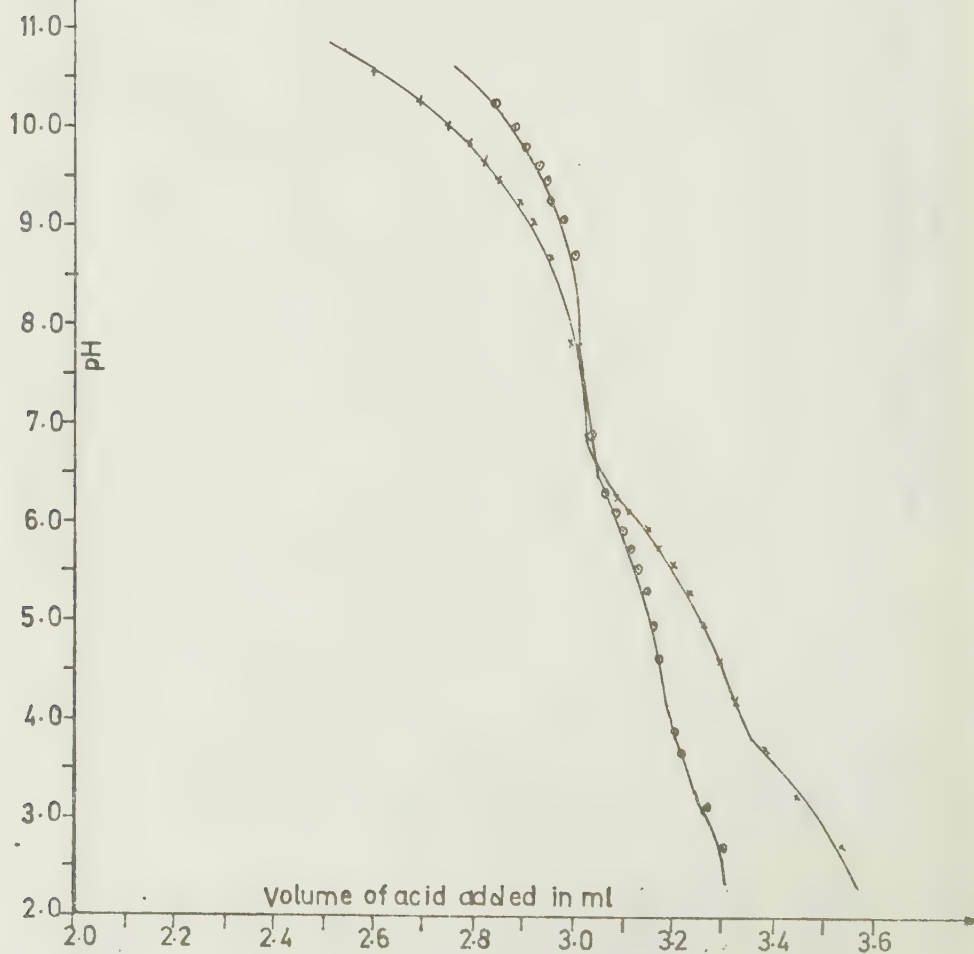


Figure 5

- 51 -

Titration curves of $[\text{Pd}(\text{phen})(\text{OH})_2]$ ($C_{\text{Pd}} = 5.0664 \times 10^{-4} \text{ M}$) in 0.01M NaOH with 0.1M HNO_3 .

I : pH scale 6 $\rightarrow$ 11, volume scale 2 ml $\rightarrow$

II: pH scale 2 $\rightarrow$ 7, volume scale 2.8 ml $\rightarrow$

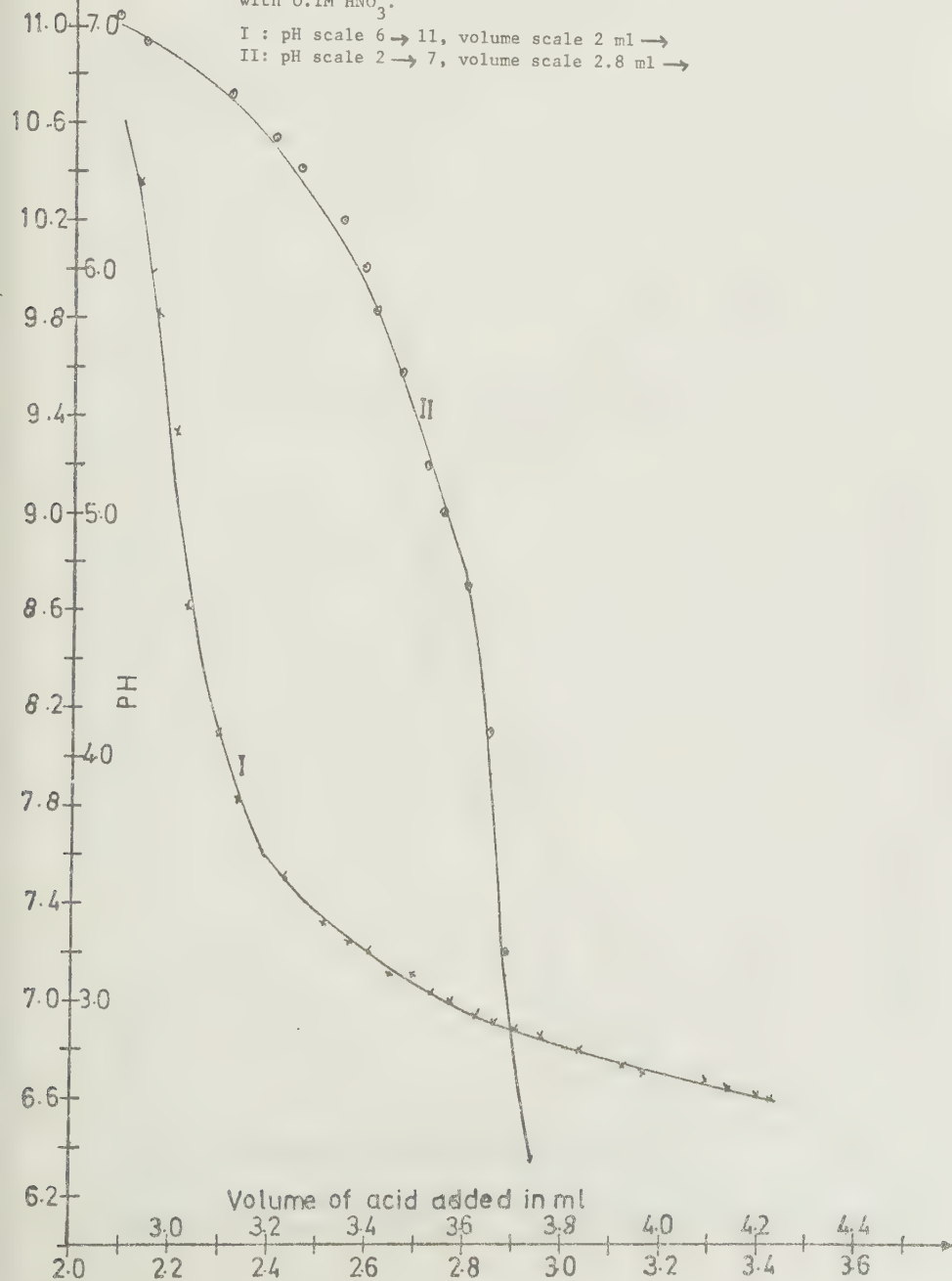
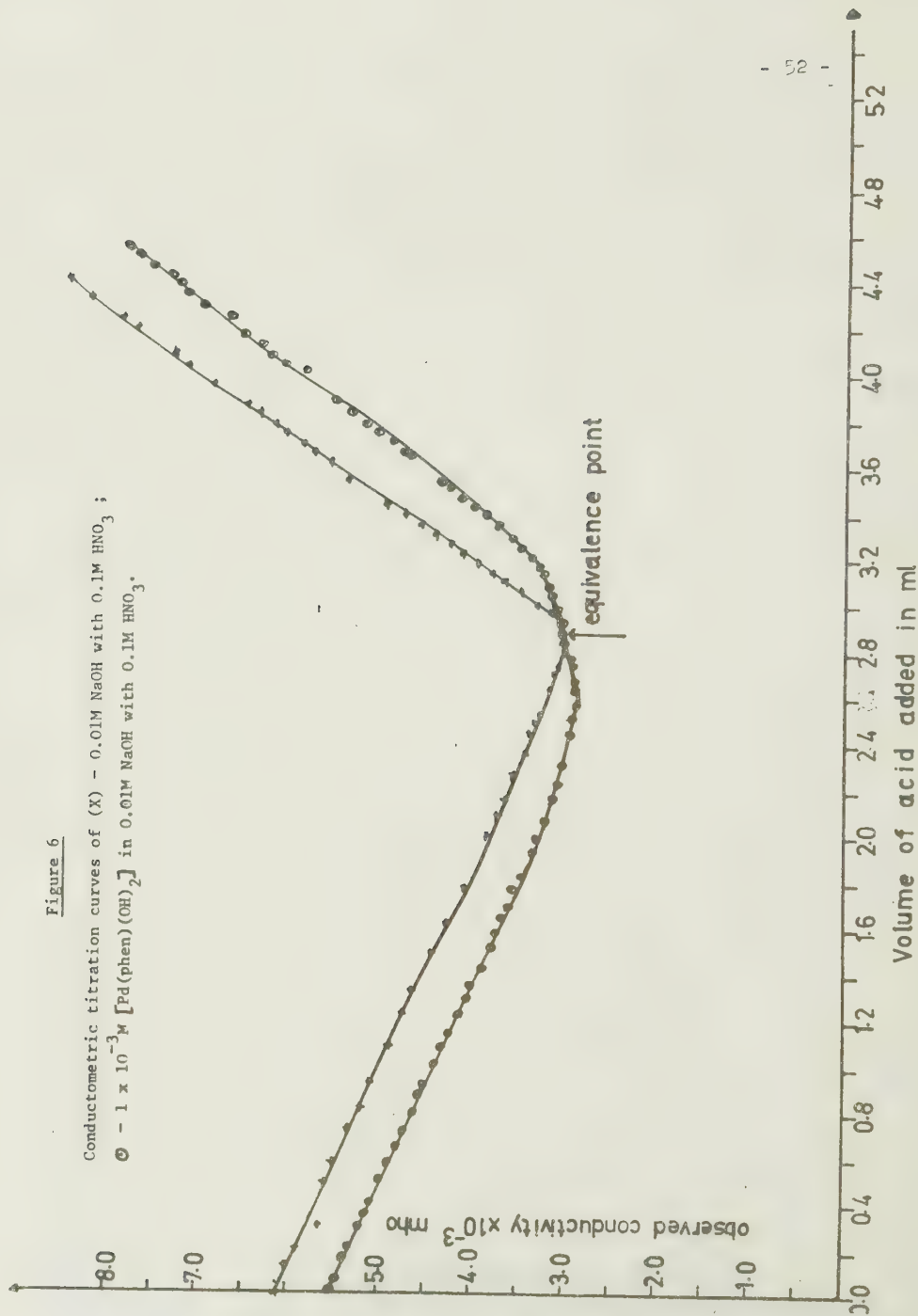


Figure 6

Conductometric titration curves of (X) - 0.01M NaOH with 0.1M HNO_3 ;
 (O) - $1 \times 10^{-3}\text{M}$ $[\text{Pd}(\text{phen})(\text{OH})_2]$ in 0.01M NaOH with 0.1M HNO_3 .



It can be seen that the maximum value of $\bar{n}$ is not 2 but 3. Figures (4,5) are a titration curve obtained from the titration of Pd(phen)(OH)_2 dissolved in sodium hydroxide solution. The corresponding formation curve is shown in fig. (3). It can be seen that the two titration curves give similar results. In both cases the maximum formation number is 3 indicating a co-ordination of 5 for the palladium ion since two positions are already occupied by the two nitrogen atoms of the phenanthroline molecule.

Conductivity experiments were carried out to confirm the formation of pentaco-ordinate palladium (II) ion since the additional hydroxide ion used might be due to some side reaction with the phenanthroline ligand. The conductimetric titration curve is shown in fig. (6) together with the acid-base titration carried out in the absence of the complex.

It can be seen from fig. (6) that there is difference in conductivity between the initial solution (i.e. before the addition of acid) containing Pd(phen)(OH)_2 and the one in the absence of it. The solution in the absence of the complex has a higher conductance since hydroxide ion has a much higher conductivity than any anion and hence any reaction which involves replacement of hydroxide ion by another anion will result in a lower conductance. If there were no reaction then the conductance of the two solutions should be identical since Pd(phen)(OH)_2 is a neutral molecule and hence non conducting.



From the difference in conductivity the number of additional hydroxide ion added can be calculated (see chap. III) and this difference corresponded to an addition of one molecule of hydroxide ion. The two titration curves converge since the addition of acid to the solution containing the Pd(phen)(OH)_2 results in the decomposition of the trihydroxo complex to the neutral Pd(phen)(OH)_2 . At the minimum of the curve, the two curves converge since at this point the ions present in solution are the same in the two solutions since Pd(phen)(OH)_2 remains undissociated. Hence conductivity measurements confirm the formation of $[\text{Pd(phen)(OH)}_3]^-$ ion i.e. the formation of a pentaco-ordinate palladium (II) ion.

The stability constants for the formation of the hydroxo complexes and the hydrolysis constants ($pK_w - \log K$) are given below.

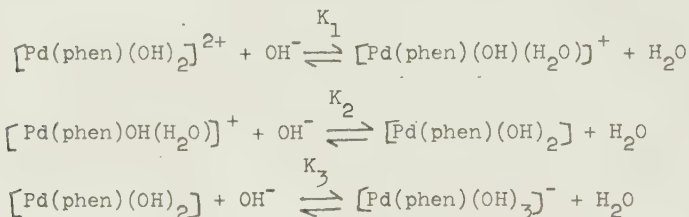


TABLE IV

$\log K_1 = 10.7$	$\pm 0.1,$	$\log K_{1\text{hyd}} = 3.3$
$\log K_2 = 8.1$	$\pm 0.1,$	$\log K_{2\text{hyd}} = 5.9$
$\log K_3 = 4.4$	$\pm 0.1,$	$\log K_{3\text{hyd}} = 9.6$

Table V ¹² gives the values for the formation of hydroxo complexes from the tetraaquo ion and also some values for the hydrolysis constants of some platinum (II) and cobalt (III) ¹² complexes.

TABLE V

	$\log K_{1\text{hyd}}$	$\log K_{2\text{hyd}}$
cis- $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2]^{3+}$	4.45	6.8
cis- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$	6.06	8.19
cis- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	5.95	8.05
cis- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$	5.56	7.32
cis- $[\text{Pt}(\text{py})_2(\text{H}_2\text{O})_2]^{2+}$	3.9	6.4
$[\text{Pt}(\text{dip})(\text{H}_2\text{O})_2]^{2+}$	4.7	5.7

cis- $[\text{PtA}_2(\text{H}_2\text{O})_2]^{2+}$ same K_1 and K_2 as NH_3 for $A = \text{Me}(\text{NH}_2)_2$, $\text{Et}(\text{NH}_2)_2$, en

	$\log \beta_1$	$\log \beta_2$	
$[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ (25)	13.0	25.8	pH titration
	12.4	26.5	spectrophotometry.

From the hydrolysis constants of palladium (II) it can be seen that $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ is 10^2 less acidic than the tetraaquo ion. This is a common feature of a lot of complexes where the aquo ion is stabilised by ligand substitution. Since phenanthroline and dipyridyl have very similar properties, one would expect the behaviour of either of the ligand to be representative of both except where steric factors intervene. The hydrolysis constants for $[\text{Pt}(\text{dip})(\text{H}_2\text{O})_2]^{2+}$ is lower (pK higher) than the monophenanthroline complex of palladium. This might suggest that $[\text{Pt}(\text{H}_2\text{O})_6]^{2+}$ ion would be less hydrolysed than $[\text{Pd}(\text{H}_2\text{O})_6]^{2+}$.

Trans influence and hydrolysis constants

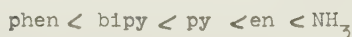
Trans influence of a ligand has been defined²⁶ as the extent to which that ligand weakens the bond trans to it in the equilibrium state of that complex. Trans influence is a ground state effect and hence the extent of trans influence can be obtained by making measurements such as the vibrational stretching frequencies of the bond trans to the ligand under study in the solid phase. It has been shown by Zumdahl and Drago that the cis influence was comparable to the trans influence although the former effect was slightly lower.

In table (VI), are given some values for the i.r. stretching frequencies of Pt - Cl and Pd - Cl of some Pt (II) and Pd(II) complexes.

TABLE VI

Complex	Pt - Cl stretching frequencies(26)	Pd - Cl (both asymmetric and symmetric frequencies (27)
cis-[M(II)(phen)Cl ₂]	347	353, 346 s
[M(II)(bipy)Cl ₂]	345	354, 342
cis-[M(II)(py) ₂ Cl ₂]	336	342, 333
[M(II)(en)Cl ₂]	325	307, 296
cis-[M(II)(NH ₃) ₂ Cl ₂]	321	327, 306

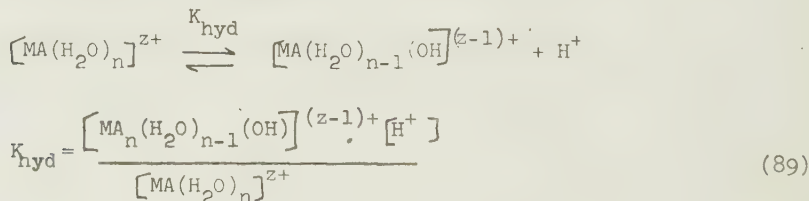
Since Pd-phenanthroline complexes are necessarily cis, only the cis complexes have been chosen for the data in table (V) and table (VI). It can be seen from table (V) that the following order for the trans influence is obtained



In the case of Pd(II) the order for en and NH₃ are interchanged.

The effect of trans influence would be to weaken the ligand trans to it, in other words to lower the stability of the bond opposite it.

Hydrolysis is the formation of hydroxo complexes from the corresponding aquo complexes



Hydrolysis reaction involves the weakening of the O-H bond. A good trans influencing ligand would weaken the M - O bond thereby strengthening the O - H bond. Hence hydrolysis constants would be lower for ligands high in the trans influencing series.

From the data given in table (V) for the hydrolysis constants, the following order of increasing hydrolysis (inverse of trans order) is obtained.

For Co(III) phen $> \text{NH}_3 > \text{en}$
 Pt(II) py $> \text{dip} > \text{NH}_3 > \text{en}$

To find if palladium (II) complexes also obeyed the above order, a rough value for the hydrolysis constant for $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ was obtained by measuring the pH of a solution $\text{Pd}(\text{en})\text{Cl}_2$ from which Cl^- had been removed by the addition of AgNO_3 . pK for such a solution was $\simeq 6$. From the work of L. Rasmussen and C.K. Jørgensen it would seem that the $[\text{Pd}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$ complex did not show any appreciable hydrolysis. $[\text{Pd}(\text{dien})(\text{H}_2\text{O})_2]^{2+}$ has also been found to have $\text{pK} \simeq 6$.

Hence for Pd (II) complexes the hydrolysis constants have order similar to that of Pt i.e.

phen $> \text{NH}_3 \simeq \text{en}$

The hydrolysis constants obtained for Pd(II) and Pt(II) do reflect the trans influence.

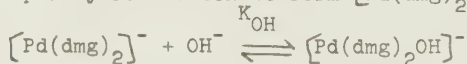
Penta co-ordinate $[\text{Pd}(\text{phen})(\text{OH})_3]^-$

The addition of hydroxide ion to $\text{Pd}(\text{phen})(\text{OH})_2$ to form $[\text{Pd}(\text{phen})(\text{OH})_3]^-$ is a surprising result because this would mean a stereochemical change and palladium (II) complexes have been known to form predominantly square planar complexes. The change in stereochemistry should result in a change in spectrum (as was found for the pentammine effect of Cu(II)) and the spectra of $\text{Pd}(\text{phen})(\text{OH})_2$ and $[\text{Pd}(\text{phen})(\text{OH})_3]^-$ are different as will be seen later on the chapter on spectra of these complexes.

Five co-ordination complexes are relatively rare compared to either the four-co-ordinated or six-co-ordinated complexes. In solution, compounds having a co-ordination number of five have frequently been postulated as intermediates in both the reactions of octahedral complexes by SN_2 mechanism. A six-co-ordination complex is theoretically more stable than the corresponding penta co-ordinated complexes. Hence if metal ions which normally form six-co-ordinated complexes are found to form five-co-ordinated complexes then there are generally formed due to steric reasons which prevent the hexa co-ordinated form. This is the case for complexes of the type $[M(\text{terpy})Cl]Cl$ for $M(II) = Cu, Zn$ and Cd . On the other hand d^8 (spin-paired) complexes which are normally square planar have been found to form five-co-ordinated complexes with certain ligands such as arsines. Complexes of the type $[M(II)(\text{diarsine})X]X$ where $(M=Ni, Pd, Pt)$ and $X = \text{halide ion}$ have been shown to be 5 co-ordinate in nonaqueous solvents such as nitromethane although in water $Pd(II)$ and $Pt(II)$ complexes dissociate into the corresponding four-co-ordinate, thus implying that the co-ordination number 5 is more stable for $Ni(II)$. Livingstone et al have prepared complexes of the type $[M(II)(\text{phen})_2Cl]Cl$ and they have shown that these complexes are univalent electrolytes in nitrobenzene. The fact that these complexes do not exist in water may either be due to their instability but most probably due to the replacement of chloride ions by the water molecules which are in excess.

In other words the metal-chloride bond is not very strong and can be broken by the water molecule.

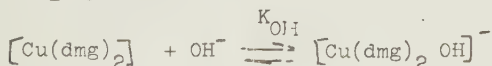
The bisdimethylglyoximato palladium (II) has also been found to take up a hydroxide ion to form $[Pd(\text{dmg})_2OH]^-$



Burger and Dyrssen²⁸ have studied the formation constant for the above reaction. They obtained a constant of $\log K_{OH} = 5.5$. This constant is ten times larger than the third constant for the formation of $[Pd(\text{phen})(OH)_3]^-$. The uptake of the fifth ligand is perhaps electrostatic in nature. Both phenanthroline and dimethylglyoxime have

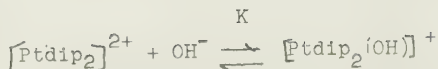
low-lying empty π^* antibonding orbitals which can overlap with the filled metal π orbitals. This would result in the lowering of the electronic density on the palladium atom thus making it slightly more positive. The electronegative hydroxide ion can thus form an ionic bond with the metal. The higher formation constant of the dimethylglyoximate complex may be due to the presence of two dimethylglyoximate ions may lead to a greater removal of charge from the metal and thus to a stronger coulombic interaction. Also the X-ray structure of this complex has been found to show that this molecule is not completely symmetrical and thus the structural deformation might facilitate the formation of the fifth bond.

In this connection it must be mentioned that dimethylglyoximate Cu(II) has also been found to take up another hydroxide ion to form $[\text{Cu}(\text{dmg})_2\text{OH}]^-$ ion²⁹.



The constant for this reaction has been found to be $\log K_{\text{OH}} = 3.2$. Since stability constants of copper (II) complexes are generally at least 10^4 times smaller than the corresponding palladium (II) complexes, the fact the observed difference in stabilities between the K_{OH} for the dimethylglyoxime complexes of the two metals is only 10^2 underlies the greater propensity for copper (II) complexes to take up the co-ordination number 5. The causes for the adoption of co-ordination 5 in the cases of copper and palladium are different. In the former it is due to the distortion of the octahedron caused by the Jahn-Teller effect that is responsible for the lower symmetry whereas in the latter case the dx^2-y^2 orbital is very antibonding thus making the palladium (II) complexes take up square planar configuration and formation of a fifth bond is energetically unfavourable. Hence the formation of a fifth bond will necessarily be weak and most probably would involve electrostatic interaction i.e. weak interaction with the metal orbital with electrons mainly concentrating on the ligand orbital.

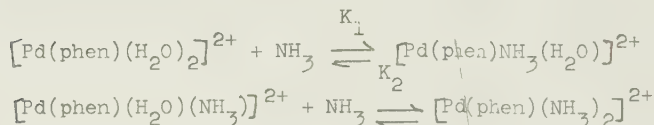
Quite recently G. Nord⁴³ has measured the hydrolysis constant of bis(2, 2'-dipyridyl) platinum (II) and found $\text{PK}_{\text{hyd}} = 9.2$ i.e. $\log K = 4.76$



IV(2) Formation of diamminomonophenanthroline palladium (II) ion

Figure (7) shows the titration curves obtained for the titration of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ in the presence of ammonium nitrate with 0.1 Molar sodium hydroxide solution. Calculation of $\bar{n}$ ignoring the hydrolysis of diaquophenanthroline palladium (II) showed that $\bar{n}$ and pNH_3 (-log of free ammonia concentration) depended on the total palladium concentration used. Figure (8) shows the formation curve taking into account the hydrolysis of the aquo ion.

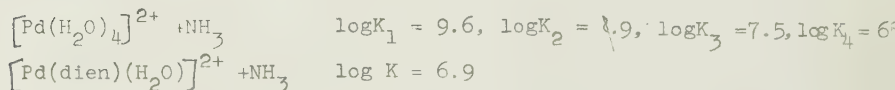
The formation constants for the following reactions



(The dissociation constant for ammonia was found to be $\text{p}K = 9.27$) were found to be $\log K_1 = 7.45 \pm 0.1$,
 $\log K_2 = 6.3 \pm 0.1$

Table (VII) gives the formations constants obtained by L. Rasmussen and C.K. Jørgensen¹⁸ for the tetrammine palladium (II) and also the formation²¹ of monoammine diethylenetriamine palladium(I)

TABLE VII



Before making any comparison, it must be pointed out that the values cited in table (VII) were determined at 1M ionic strength (using NaClO_4) whereas the values obtained in this work was in dilute solution containing nitrate ion. If the nitrate ions present in solution formed nitrate complexes then the constants obtained would be lower than the actual constants. Since ammonia is neutral

Figure 7

Titration curves of $[\text{Pd}(\text{phen})(\text{NO}_3)_2]$ (C_{Pd}) 0.01M HNO_3 and $0.01\text{M NH}_4\text{NO}_3$ with 0.01M NaOH .

1 : $C_{\text{Pd}} = 7.4960 \times 10^{-4}\text{M}$; 2 : $C_{\text{Pd}} = 4.9774 \times 10^{-4}\text{M}$; 3 : $C_{\text{Pd}} = 2.5442 \times 10^{-4}\text{M}$

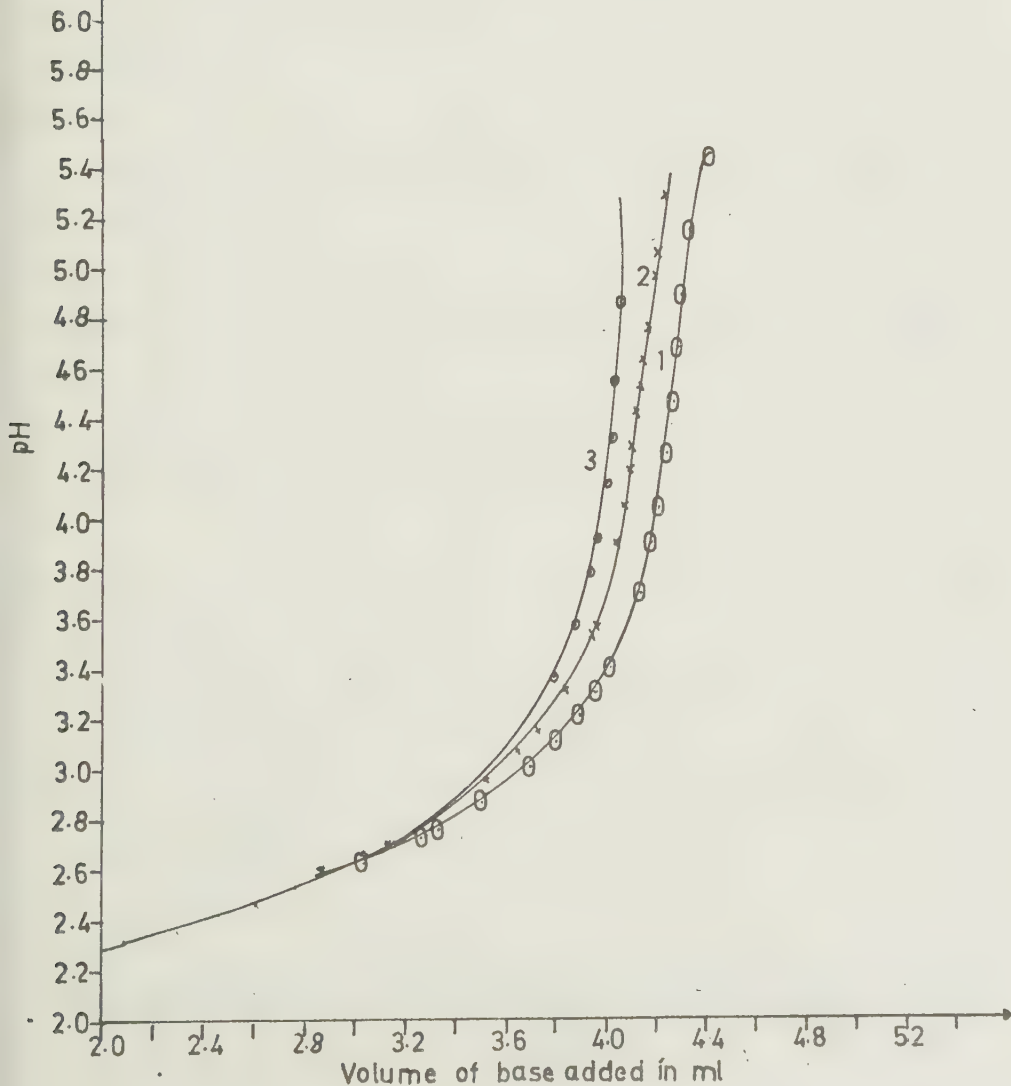
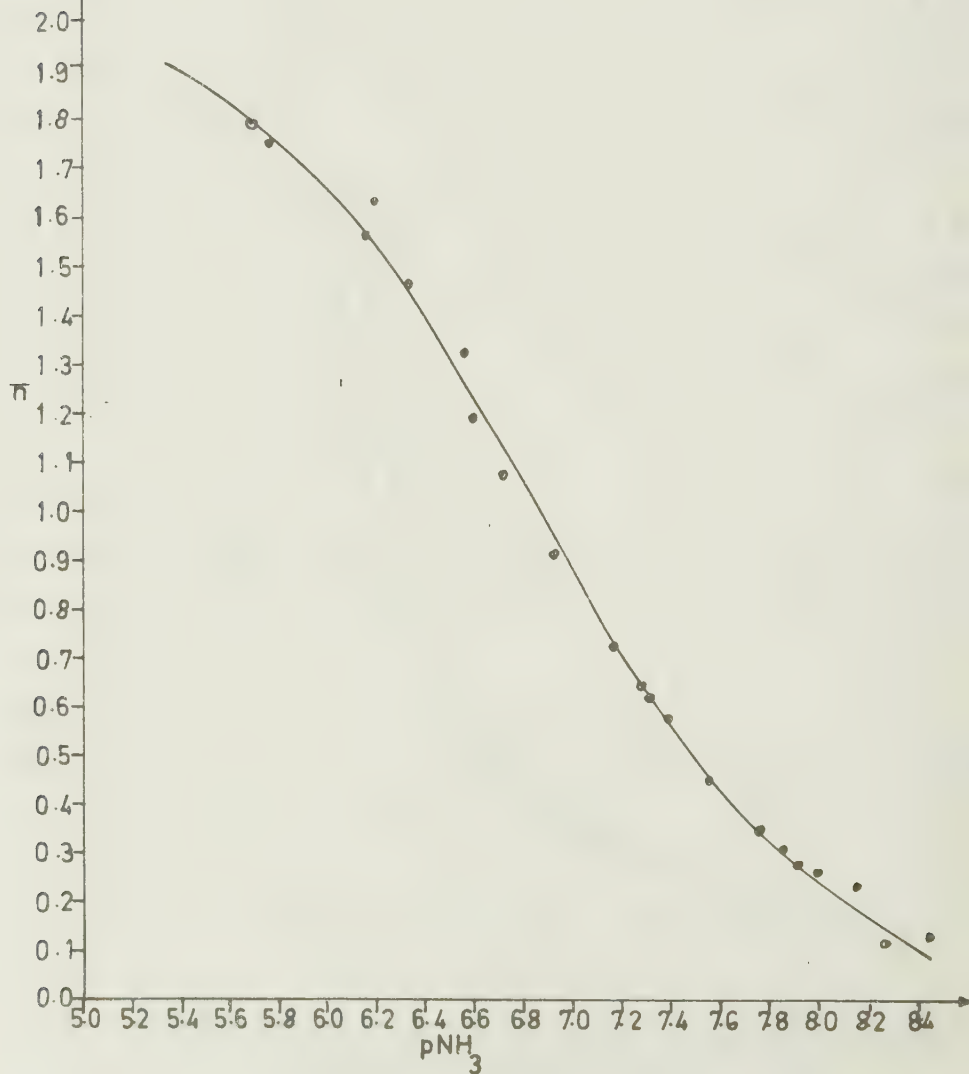


Figure 8

Formation curve for $[\text{Pd}(\text{phen})(\text{NH}_3)_2]^{2+}$.

ligand the effect of change in ionic strength on the stability constants would not be very great. On this basis, the values found in this work are comparable with the values listed in table (VII). There is no significant weakening of the bonds opposite the phenanthroline ligand due to the strong palladium-phenanthroline bond. On the other hand the presence of phenanthroline as mentioned earlier might have strengthened the other two ligands but this effect is either very small or it is masked by the possible formation of the nitrate complexes.

The ammine formation could not be followed spectrophotometrically because of the close similarity between the spectra of the diaquo-phenanthroline palladium (II) and diamminophenanthroline palladium (II) complexes.

Calculations on the formation constants of the amines did not indicate any formation of $[\text{Pd}(\text{phen})(\text{NH}_3)_3]^{2+}$ i.e. co-ordinate number 5 as was observed for the hydroxo complexes. The possibility of such a complex to be formed cannot be ruled out. If such a complex were formed it would have $\log K \simeq 1$ on the basis of comparison of the fifth constant for the formation of $[\text{Cu}(\text{NH}_3)_5]^{2+}$ ($K \simeq 0.3$) and K_{OH} for the formation of $[\text{Cu}(\text{dmg})_2\text{OH}]^-$ and $[\text{Pd}(\text{dmg})_2\text{OH}]^-$.

(3) The formation of $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$

Although the position of the maxima in the spectra of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$ are the same i.e. 350 nm, the molar extinction coefficients of the two complexes are different. Hence the formation of $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$ could be studied spectrophotometrically. Figures (9, 10) show the spectra of different equilibrium mixtures of $[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$ and $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$. The formation curve is shown in figure (11).

The stability constants for the following reaction

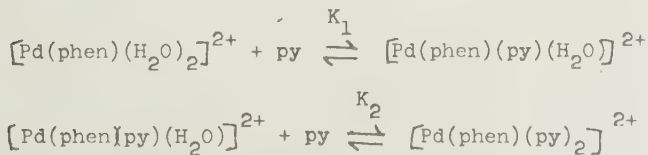


Figure 9

Absorption spectrum of $[\text{Pd}(\text{phen})\text{py}]^{2+}$ ($1.0034 \times 10^{-3} \text{ M}$) in water.

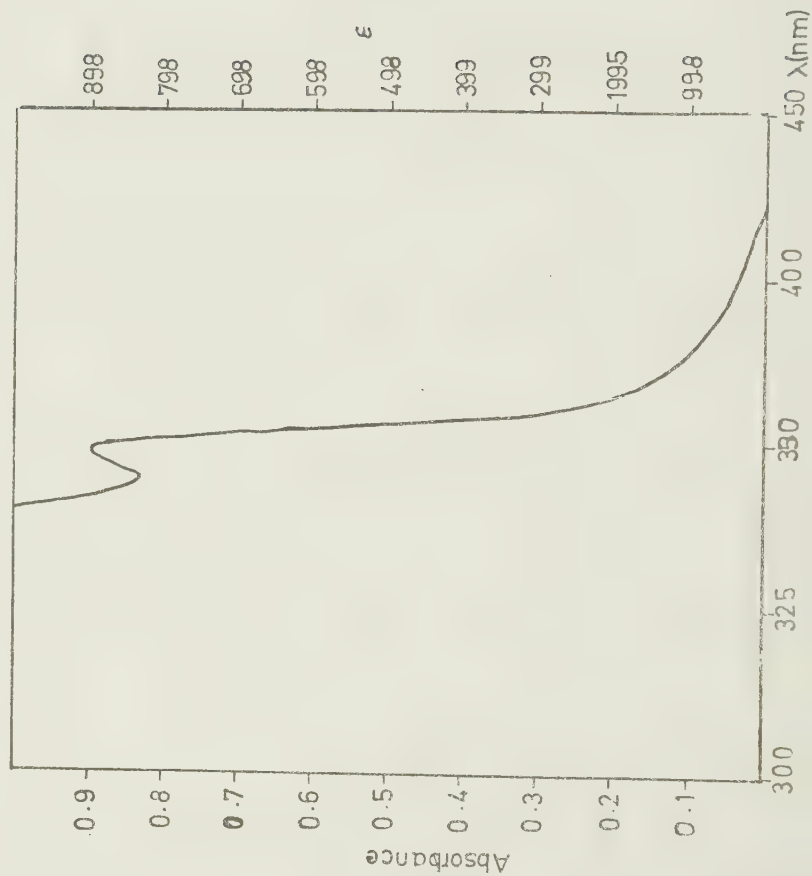


Figure 10

Absorption spectra of equilibrium solution of $[\text{Pd}(\text{phen})\text{py}]^{2+} + \text{HNO}_3$

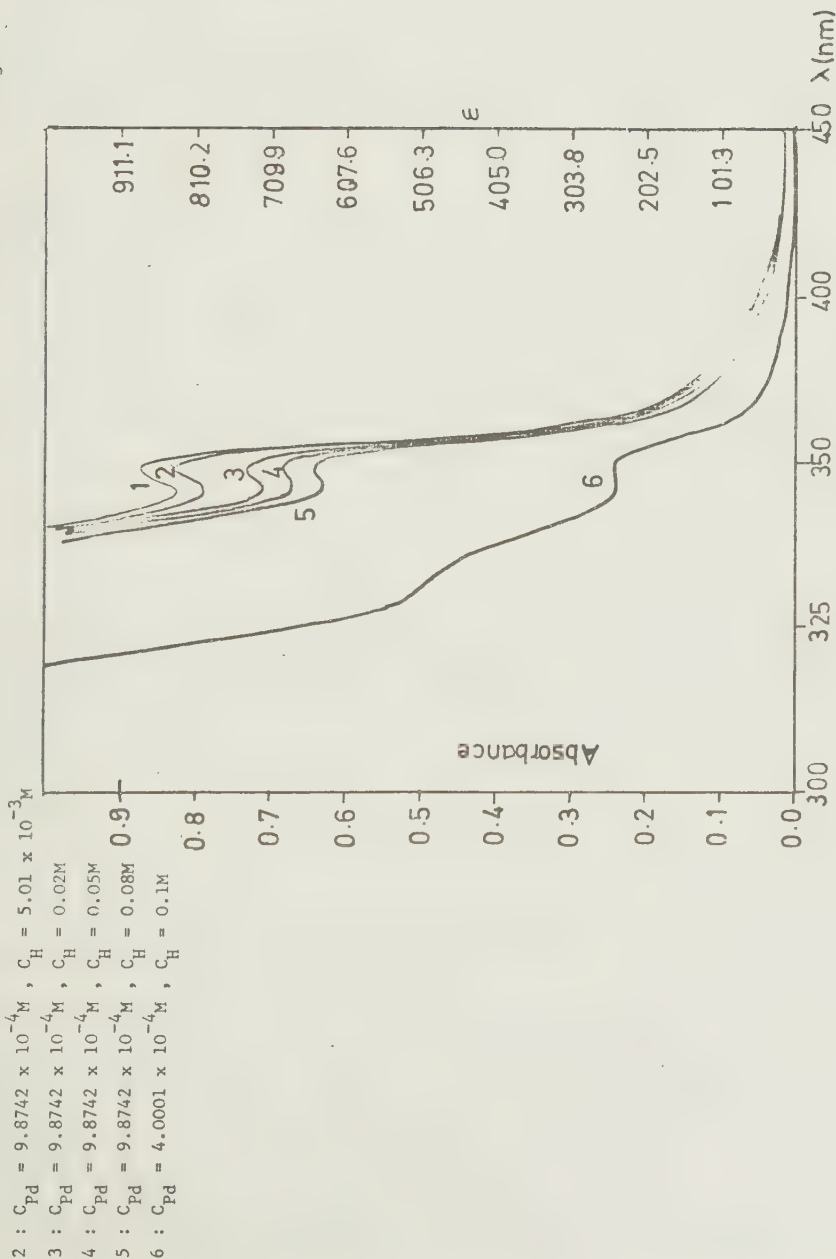


Figure 11
Formation curve for $[\text{Pd}(\text{phen})\text{py}]^{2+}$.



are $\log K_1 = 7.02$
 $\log K_2 = 6.18$

Table (VIII) gives the formation constants for the formation of $[\text{Pd}(\text{py})_3(\text{H}_2\text{O})]^{2+}$ and $[\text{Pd}(\text{dien})(\text{py})]^{2+}$ together with a typical example of the formation constants of a first row transition metal ion.

TABLE VIII

$[\text{Pd}(\text{py})_2(\text{H}_2\text{O})_2]^{2+} + \text{py} \rightleftharpoons [\text{Pd}(\text{py})_3(\text{H}_2\text{O})]^{2+}$	$\log K_3 = 6.5$
$[\text{Pd}(\text{dien})(\text{H}_2\text{O})]^{2+} + \text{py} \rightleftharpoons [\text{Pd}(\text{dien})(\text{py})]^{2+}$	$\log K = 6.5$
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + \text{py} \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_n(\text{py})_{6-n}]^{2+}$	$\log K_1 = 2.52$
	$\log K_2 = 1.86$
	$\log K_3 = 1.3$
	$\log K_4 = 0.85$

It can be seen that the formation constants for the mixed pyridine-phenanthroline complexes are comparable with the values of the constants given in table (VIII) for palladium but are much larger than the values predicted by Bjerrum for pyridine complexes. According to Bjerrum's rule

$$\log K_{\text{py}} + 1.76 = 0.6 (\log K_{\text{NH}_3} + 1.76)$$

where 1.76 = logarithm of 55.5 molar of water.

Hence according to this rule, the expected constants for pyridine are $\log K_1 = 3.8$ and $\log K_2 = 3.4$.

This marked discrepancy in the observed and expected values lies in the difference between the properties of first row transition metal (II) ions which have either groupe A character i.e. hard acids or are borderline cases i.e. their acid behaviour is not typical of either hard acids or soft acids and palladium (II) which is a typical soft acid. According to the theory of soft and hard acids and bases

hard acids prefer hard bases and soft acids soft bases. The palladium which is well known for its group B characteristic, shows a high affinity for the soft base pyridine. Another way of looking at this problem is that palladium-pyridine bond has more covalent character than pyridine complexes of first row transition metals. In fact the high strength of the palladium-phenanthroline bond can also be attributed to the soft acid behaviour of palladium (II) ion. The relatively low value of $\log K_2$ compared to $\log K$ of the $[\text{Pd}(\text{dien})(\text{py})]^{2+}$ complex is most probably due to the steric hindrance of the bulky pyridine molecule.

IV(4) The formation of $[\text{Pd}(\text{phen})(\text{en})]^{2+}$

The formation of $[\text{Pd}(\text{phen})(\text{en})]^{2+}$ from $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ was studied spectrophotometrically because the high stability of this complex meant carrying out potentiometric measurements at low pH and at these pH values ($\text{pH} \leq 2$) even a small error in the measurement of pH would correspond to a large error in $[\text{H}^+]$ concentration.

The spectra of different equilibrium mixtures of $[\text{Pd}(\text{phen})(\text{en})]^{2+}$ and $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ are shown in figures (12, 13). The formation curve calculated from the spectral results is given by figure (14). Since the extinction coefficients of the diaquo complex and the ethylenediamine complex are not very different, the area under the curve was used for the calculation of individual concentrations.



$\log K$ was found to be 17.8 ± 0.1

$\log K$ for the formation of $[\text{Pd}(\text{en})_2]^{2+}$ previously found¹⁸ are

$$\log K_1 \approx 20$$

$$\log K_2 = 18.4$$

The mixed ethylenediamine-phenanthroline complex and the $[\text{Pd}(\text{en})_2]^{2+}$ have similar stabilities. This shows that in the complex $[\text{Pd}(\text{phen})(\text{en})]^{2+}$ the steric hindrance is not sufficient to result in a lowering of stability of the mixed complex. Kinetic evidence (see next chapter) shows that even in the mixed complex there is probably some

Figure 12

Absorption spectra of (1) $[\text{Pd en}(\text{H}_2\text{O})_2]^{2+}$ ($1.0006 \times 10^{-3} \text{ M}$) in 0.01 M HNO_3 and (2) $[\text{Pd}(\text{phen})\text{en}]^{2+}$ ($1.0015 \times 10^{-3} \text{ M}$) in water.

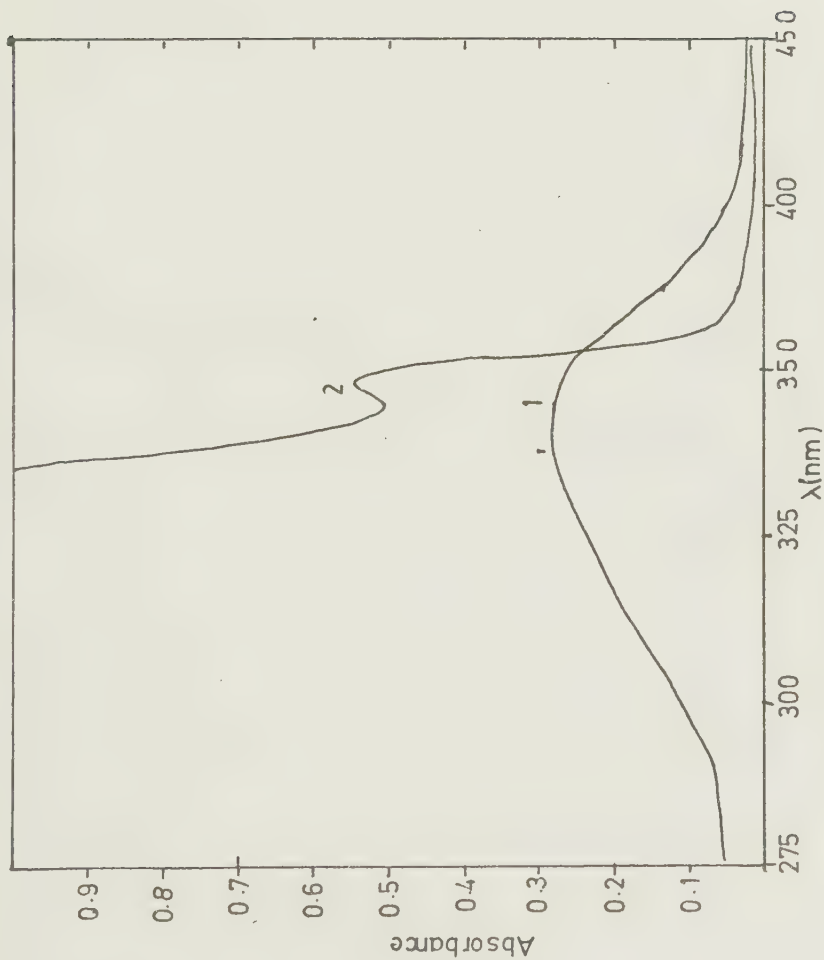


Figure 13

Absorption spectra of equilibrium solution of $[\text{Pd}(\text{phen})\text{en}]^{2+} + \text{HNO}_3$.

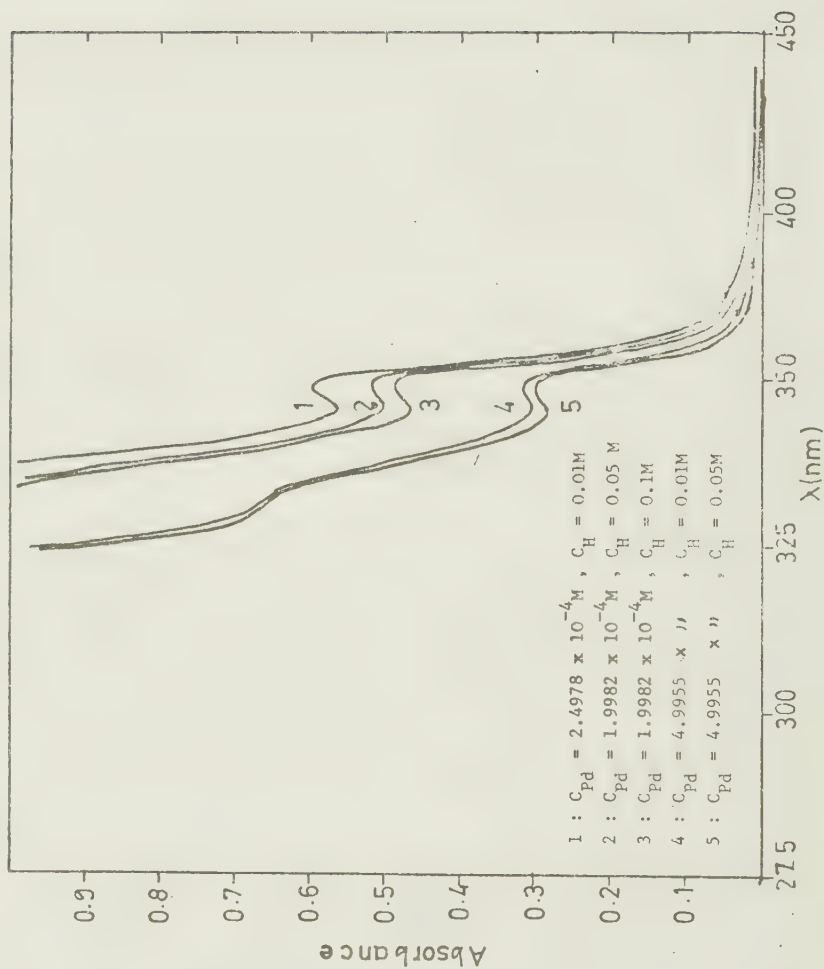
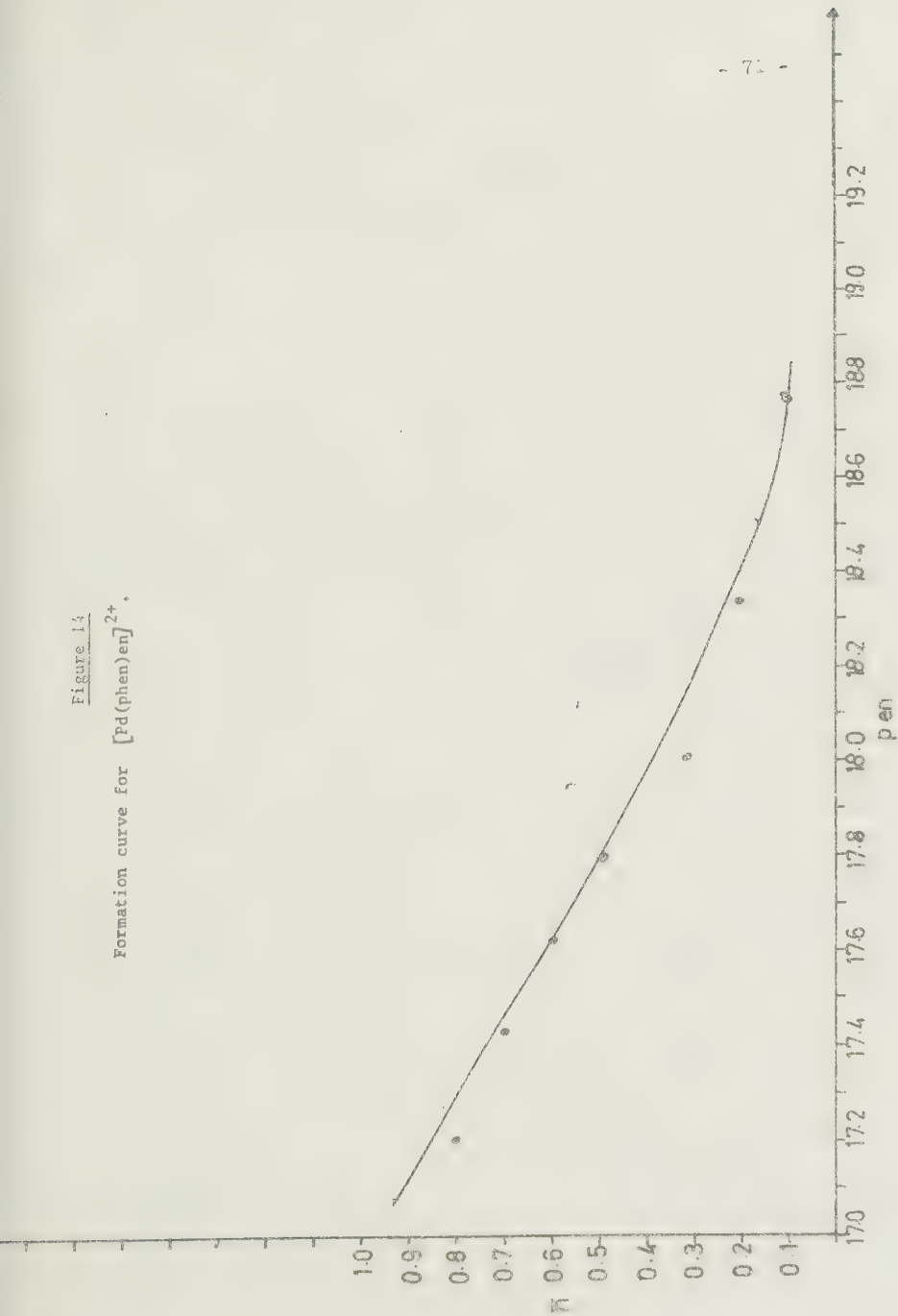


Figure 14

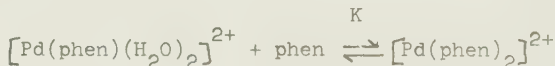
Formation curve for $[\text{Pd}(\text{phen})\text{en}]^{2+}$.



steric hindrance. The fact that steric hindrance is not always reflected in the stability constants as shown in the case of $[\text{Cu}(\text{en})_2]^{2+}$ complex where the stability constants do not show the presence of steric hindrance whereas the spectral data shows that there is some steric hindrance.

IV(5) The formation of $[\text{Pd}(\text{phen})_2]^{2+}$

The method of Job was used to establish the presence of $[\text{Pd}(\text{phen})_2]^{2+}$ in solution. Fig. (15) shows the spectra as a function of different ratios of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ to phen. This was carried out at pH 3 to prevent hydrolysis of the diaquo ion. The spectrum of $[\text{Pd}(\text{phen})_2]^{2+}$ in water is shown in figure (16). Since $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and phen, and $[\text{Pd}(\text{phen})_2]^{2+}$ absorb in the same region, the spectra obtained from the method of Job had to be resolved from the known ϵ 's for $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and phen to calculate the ϵ for $[\text{Pd}(\text{phen})_2]^{2+}$. The calculated ϵ corresponded to that obtained from the measured ϵ for $[\text{Pd}(\text{phen})_2]^{2+}$ in water (see table IX). The method of Job also showed that only $[\text{Pd}(\text{phen})_2]^{2+}$ is formed and not more than two phenanthrolines are bonded to the metal. The spectra of $[\text{Pd}(\text{phen})_2]^{2+}$ as can be seen from figure (16) is different from both $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and phen, and hence the formation for the bis(phenanthroline) palladium (II) complex could be conveniently studied by carrying out spectral measurements. Fig. (17) shows the spectra of the equilibrium mixtures of mono and bis phenanthroline complexes at different pH. The stability constant for the formation of $[\text{Pd}(\text{phen})_2]^{2+}$ referring to the following equation :



is $\log K = 9.4 \pm 0.1$ (Figure 18)

The monophenanthroline complex is formed even at 5M HNO_3 . The monophenanthroline complex is as strong as the monoethylenediamine complex ($\log K \approx 20$) and the second constant for the formation of $[\text{Pd}(\text{en})_2]^{2+}$ is 18.

Figure 15

Absorption spectra of solutions containing different ratios of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and phenanthroline.

1:1, 1:2, 2:1 and 1:3 at half the concentration of Table IX

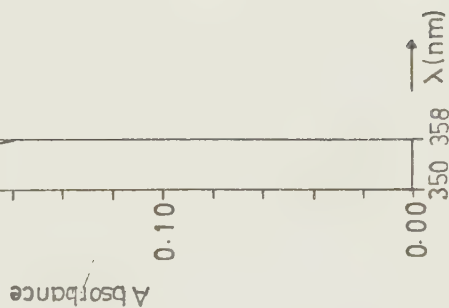


Figure 16

Absorption spectra of solution of (1) $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ ($1.0062 \times 10^{-3}\text{M}$),
 (2) $[\text{Pd}(\text{phen})_2]^{2+}$ ($2.8675 \times 10^{-4}\text{M}$), (3) Phen ($1.0045 \times 10^{-3}\text{M}$) in 0.01M HNO_3 .

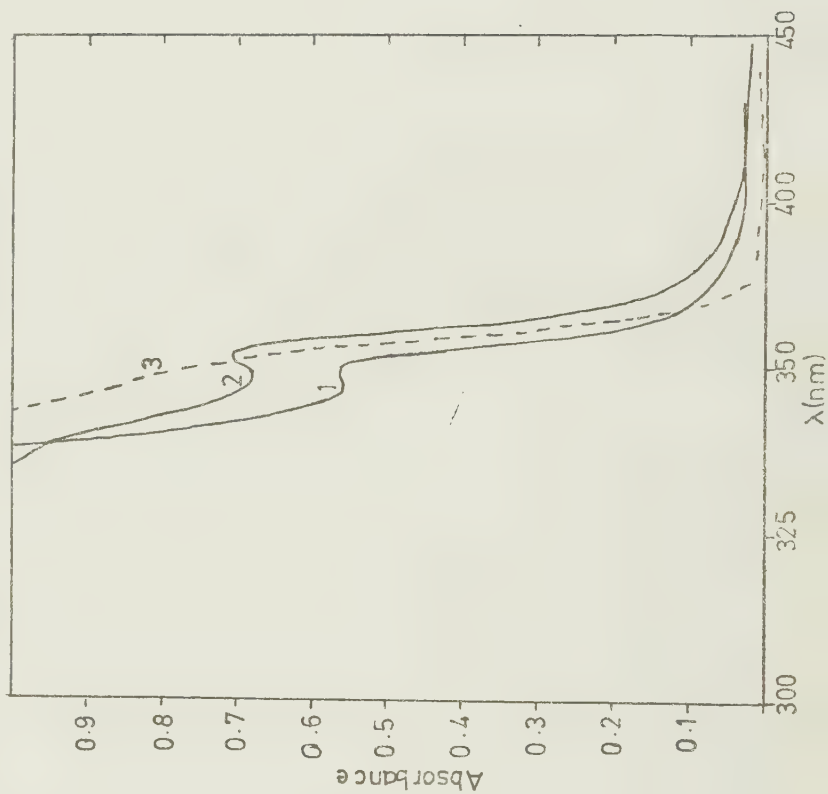


Figure 17

Absorption spectra of equilibrium solutions of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+} + \text{phen}$
(using 4 cm cells).

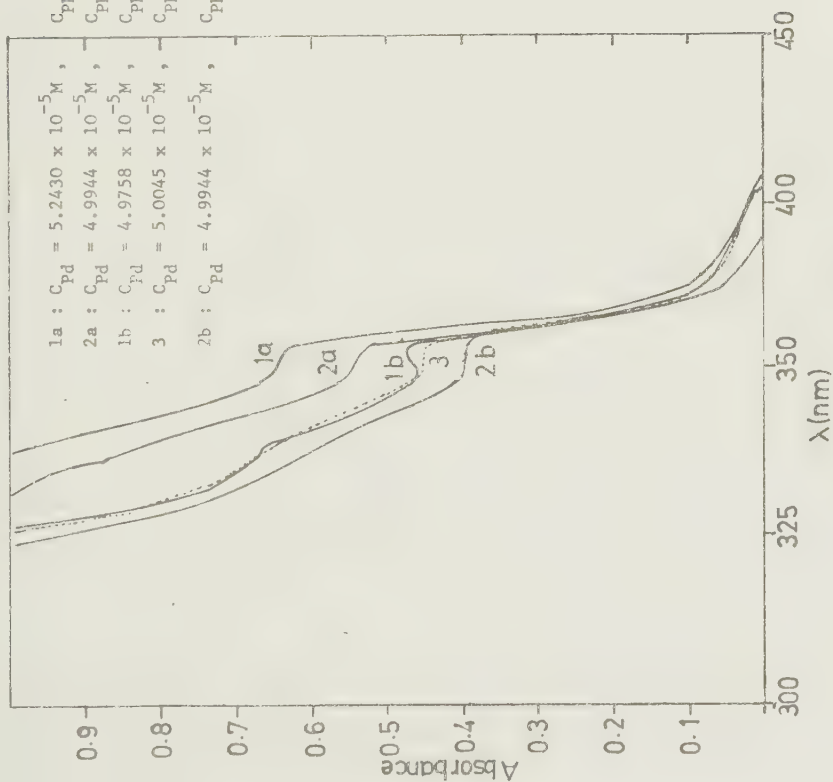


Figure 18
Formation curve for $[\text{Pd}(\text{phen})_2]^{2+}$.

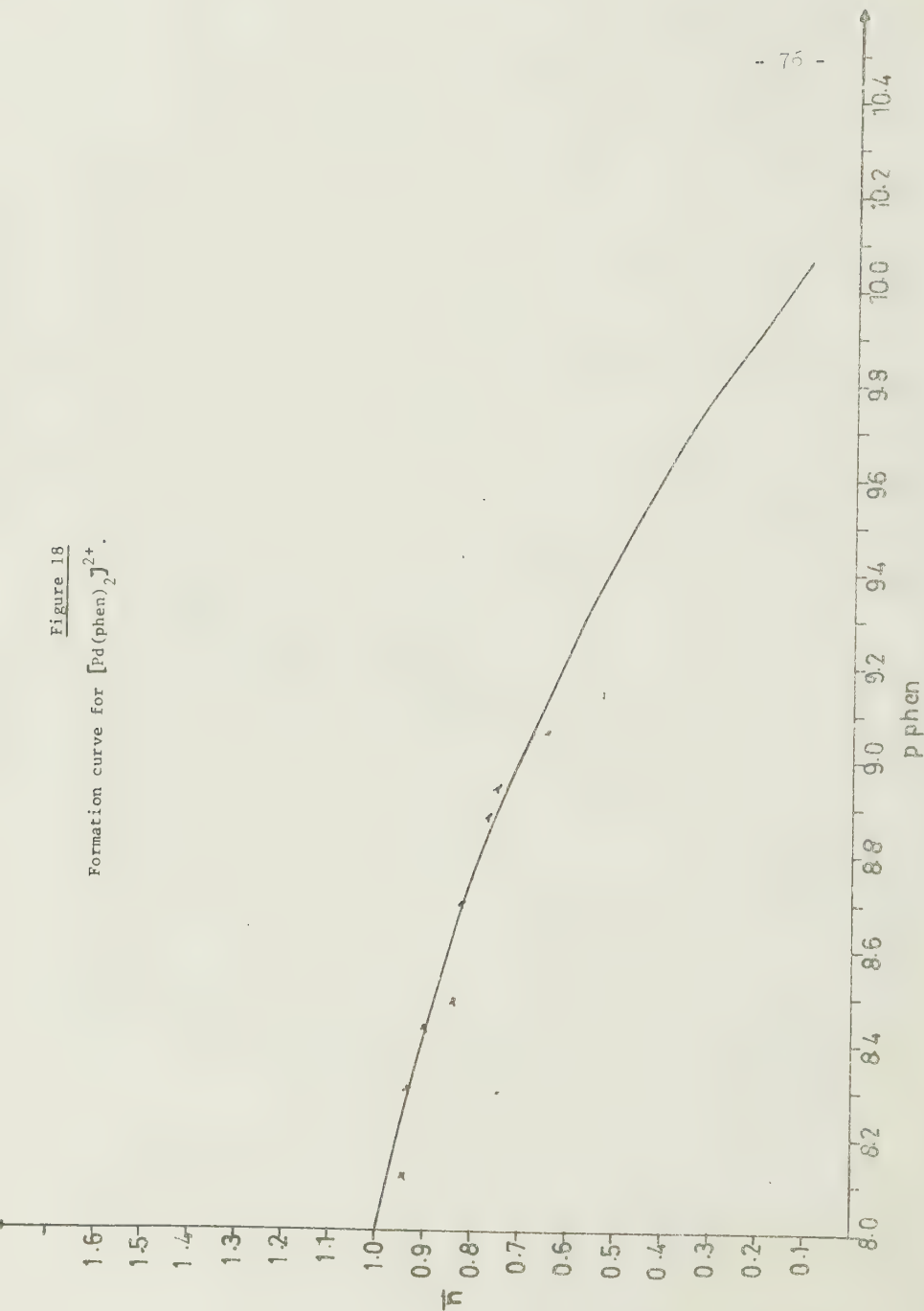


TABLE IX

$T_{\text{Pd}}/T_{\text{phen}}$	$T_{\text{Pd}}(\text{M})$ $\times 10^{-4}$	$T_{\text{phen}}(\text{M})$ $\times 10^{-4}$	Abs. meas.	Abs. calc.	Δ	ϵ_2^*
3:1	3.7585	1.2516	0.352	0.219	0.132	1990
2:1	3.3827	1.6270	0.403	0.223	0.179	2030
1:1	2.5057	2.5031	0.492	0.233	0.259	1970
1:2	1.6281	3.3792	0.412	0.242	0.17	1970
1:4	1.0023	4.0050	0.368	0.249	0.119	2120

ϵ_2 measured from a solution of $\text{Pd}(\text{phen})_2^{2+}$ in water = 2000

Average $\bar{\epsilon}_2$ from the table = 1990

T_{Pd} = total concentration of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ in moles per litre

T_{phen} = total concentration of phenanthroline in moles per litre

Δ = difference between the observed absorption and the calculated absorption

Abs.meas. = observed optical density at $\lambda_{\text{max}} = 354 \text{ nm.}$

Abs.calc. = calculated optical density assuming no formation of $\text{Pd}(\text{phen})_2^{2+}$ complex

ϵ_2 = Molar extinction coefficient calculated from the measured absorption and using the known (previously measured) extinction coefficients of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and phenanthroline

* All these measurements were made using a Beckmann spectrophotometer whereas all the other spectra recorded in this work have been made using a Unicam Sp 8000. The extinction coefficients obtained from the Beckmann instrument are all lower than the corresponding ones obtained with the Unicam.

The second constant for the bis(phenanthroline) complex should also be about the same. This great difference in the stability of the bis(phenanthroline) complex is undoubtedly due to steric hindrance owing to the rigidity of the two phenanthroline molecules. This

steric hindrance is demonstrated in both it's kinetic and spectral property (both of these properties will be discussed under their respective headings).

Copper (II) complexes of ethylenediamine and phenanthroline behave in an analogous way

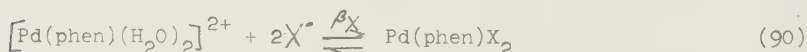
	$\log K_1^*$	$\log K_2^*$	$\log K_3^*$
Cu(II) + en	10.72	9.31	
Cu(II) + phen	9.08	6.68	5.95

* ref (12)

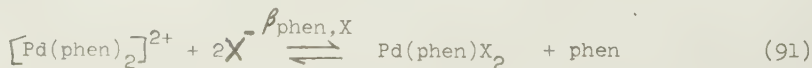
V(6) The stabilities of halocomplexes of $[\text{Pd}(\text{phen})]^{2+}$

All the complexes of the type $\text{Pd}(\text{phen})\text{X}_2$ (where X = halide ion) are very insoluble in water due to the complexes being neutral. Even trace amounts of halide ions is sufficient for the precipitation of these complexes from any monophenanthroline palladium (II) complexes.

The stability for the following reaction



were calculated from the measurement of $\beta_{\text{phen},\text{X}}$ of the following reaction



and the constant for the formation of the bisphenanthroline complex K_{phen}

$$\beta_{\text{X}} = \beta_{\text{phen},\text{X}} \times K_{\text{phen}} \quad (92)$$

Phenanthroline concentration in equation (91) was determined spectrophotometrically as $[\text{Fe}(\text{phen})_3]^{2+}$ and the amount of $\text{Pd}(\text{phen})\text{X}_2$ was determined gravimetrically.

	$\log \beta$
$[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+} + \text{Cl}^-$	6.9 ± 1
$[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+} + \text{Br}^-$	8.7 ± 0.1

Table (X) gives the values of formation of chloro and bromo complexes

TABLE X *

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_1 + \log K_2 + \log K_3 + \log K_4$
$[\text{Pd}(\text{H}_2\text{O})_4]^{2+} + \text{Cl}^-$	4.47	3.29	2.41	1.37	7.76
$[\text{Pd}(\text{H}_2\text{O})_4]^{2+} + \text{Br}^-$	5.17	4.25	3.3	2.22	9.42

* Reference (32)

The constants for the formation of $\text{Pd}(\text{phen})\text{Cl}_2$ and $\text{Pd}(\text{phen})\text{Br}_2$ conform both with the usual order for B-type complexes i.e. $K_{\text{Br}} > K_{\text{Cl}}$ and the order obtained for the formation of tetrahalo palladium (II) complexes.

The constants for the formation of $\text{Pd}(\text{phen})\text{X}_2$ obtained are greater than the corresponding formation of $[\text{PdCl}_4]^{2-}$ i.e. $\log K_3 + \log K_4$. This is not surprising since part of the formation constant is due to the coulombic attraction between the metal ion and the ligand. In the case of monophenanthroline palladium (II) complex the metal has a charge of 2+ and thus would react more strongly with the negative halide ion than in the case of $\text{Pd}(\text{X}_2)(\text{H}_2\text{O})_2$ where the complex is neutral. To compare the $\text{Pd}(\text{phen})\text{X}_2$ complexes with $[\text{PdX}_4]^{2-}$ complexes, the formation constant for the addition of two halide ions i.e. $\log K_1 + \log K_2$ of the latter must be used taking into account the statistical correction factor i.e. $\log \frac{K_{n+1}}{K_n} = \log \frac{n(N-1)}{(n+1)(N-n+1)}$

This would give a value of ≈ 6 for $\log \beta_2$. The observed value is ten times bigger. This increase in stability might be attributed to the fact that the phenanthroline molecule has empty π orbitals which can

overlap with the filled d orbitals of palladium. This would have the effect of making the charge on the metal more positive and thus would result in an increase in the bond strength.

The formation of bromo complexes on the other hand is not significantly strengthened. This might be due to the fact that the bromide ion being bigger than the chloride ion will give rise to more steric repulsion and thus the calculated theoretical value is larger because of the neglect of steric overcrowding.

Hence both the chloro and bromo complexes of $[\text{Pd}(\text{phen})]^{2+}$ show higher stability than expected.

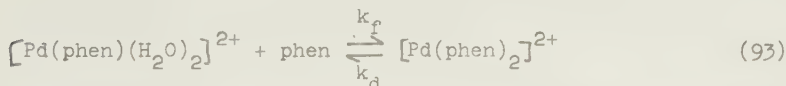
CHAPTER V

THE KINETICS OF FORMATION OF MIXED PHENANTHROLINE COMPLEXES

In the study of the formation constant for bis(phenanthroline) palladium (..I), it was found that the development of colour (from pale yellow to bright yellow) indicating the formation of the bis complex was noticeably slow. Since the equilibrium constant for the formation indicated steric strain in the molecule, a kinetic study was undertaken to see if the rate of the reaction reflected the steric strain.

It was not our aim to find the mechanism of the formation of this complex and hence no attempt has been made to postulate the reaction paths involved.

The following reaction was studied spectrophotometrically.



in acid media ($\text{pH} < 2$). The rates were measured at different pH. The upper value for the pH chosen ($\text{pH} = 2$) was to prevent the formation of hydroxo complexes. Because of the limited solubilities of both the mono and the bisphenanthroline complexes, only dilute solutions ($C_{\text{Pd}} = 5 \times 10^{-5} \text{M}$) could be used especially when studying at pH near 0. The spectra were measured in the near u.v. region and the formation of biscomplex was followed by measuring the optical densities at $\lambda = 354 \text{ nm}$. At this wavelength all the three species present in solution absorb but since their molar extinction coefficients are known, the individual concentrations could be evaluated. 4 cm quartz cells were used for absorption measurements in all the cases except at pH 2 when because of the larger extinction coefficient of $[\text{Pd}(\text{phen})_2]^{2+}$ (since the reaction is almost complete) 1 cm cells were used.

The experimental procedure used was similar to that used in the study of the formation constant of the bis complex. Solutions containing $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and phen in known acid strength were mixed in the ratio 1:1, 1:2 and 1:3 and the spectra measured as a function of time.

$$\text{since } K_{\text{phen}} = \frac{[C_2]}{[C_1][\text{phen}]}$$

$$[\text{phen}] = [\text{phen}]_T \times \frac{K_a}{[H^+] + K_a} \quad (100)$$

where K_{phen} = formation constant of the bis complex
and K_a = dissociation constant of phenanthroline

since $[H^+] \gg [\text{phen}]$ it can be considered as being virtually constant throughout the reaction.

$$\frac{k_f}{k_d} = \frac{[C_2]_{\text{eq}}}{[C_1]_{\text{eq}}[\text{phen}]_{\text{eq}}} \cdot \frac{K_a}{[H^+] + K_a} \quad (101)$$

$$= \frac{K_{\text{phen}} \cdot K_a}{[H^+] + K_a} \quad (102)$$

$$k_d = \frac{k_f \cdot ([H^+] + K_a)}{K_{\text{phen}} \cdot K_a} \quad (103)$$

$$\frac{d[C_2]}{dt} = k_f [C_1][\text{phen}]_T - \frac{k_f}{K_{\text{phen}} \cdot K_a} ([H^+] + K_a) \quad (104)$$

since total palladium concentration, $C_{\text{Pd}} = [C_1] + [C_2]$

$$[C_1] = (C_{\text{Pd}} - [C_2])$$

$$\text{and } [\text{phen}]_T = C_{\text{phen}} - [C_2]$$

where C_{phen} = total initial concentration of phenanthroline.

$$\frac{d[C_2]}{dt} = k_f \left[(C_{\text{Pd}} - [C_2])(C_{\text{phen}} - [C_2]) - \frac{[H^+] + K_a}{K_{\text{phen}} K_a} \cdot [C_2] \right] \quad (105)$$

For a particular kinetic run, $[H^+] = \text{constant}$

$$\text{By putting } \frac{[H^+] + K_a}{K_{\text{phen}} \cdot K_a} = A$$

$$\frac{d[C_2]}{dt} = k_f [C_{Pd} C_{Phen} - [C_2] (C_{phen} + C_{Pd} + A) + [C_2]^2] \quad (106)$$

$$\int \frac{d[C_2]}{C_{Pd} C_{phen} - [C_2] (C_{phen} + C_{Pd} + A) + [C_2]^2} = k_f \int dt \quad (107)$$

the left hand side of the integral is of the form $\frac{dx}{a + bx + cx^2}$ and it's solution taken from the Physical Handbook of Chemistry and Physics, 54th Edition (1973-74), (CRC press), page A-120, No. 120 is :

$$\frac{1}{\sqrt{q}} \ln \frac{2cx + b - \sqrt{q}}{2cx + b + \sqrt{q}} \quad \text{where } q = b^2 - 4ac$$

In our case $a = C_{Pd} C_{phen}$

$b = -(C_{Pd} + C_{phen} + A)$

$c = -1$

Plotting a graph of $\ln \frac{2cx + b - \sqrt{q}}{2cx + b + \sqrt{q}}$ against time , the second order formation constant k_f is obtained from the slope of the graph.

Figure (19) gives a typical evolution of spectra as a function of time and figure (20) gives the corresponding plot for the rate constant

Table (XI) gives the rate constants obtained together with the pH.

Figures (20,22) show that the second order plot is well obeyed.

Figure 19

Absorption spectra for the formation of $\text{Pu}(\text{phen})_2^{2+}$ from
 $\text{Pu}(\text{phen})(\text{H}_2\text{O})_2^{2+}$ and phen at pH 2 as a function of time .

$C_{\text{Pu}(\text{phen})(\text{H}_2\text{O})_2^{2+}} = 2.4995 \times 10^{-4} \text{M}$, $C_{\text{phen}} = 2.4999 \times 10^{-4} \text{M}$

(1) $t = 2 \text{ mins}$, (2) $t = 10 \text{ mins}$, (3) $t = 20 \text{ mins}$, (4) $t = 25 \text{ mins}$,

(5) $t = 45 \text{ mins}$, (6) $t = \infty$

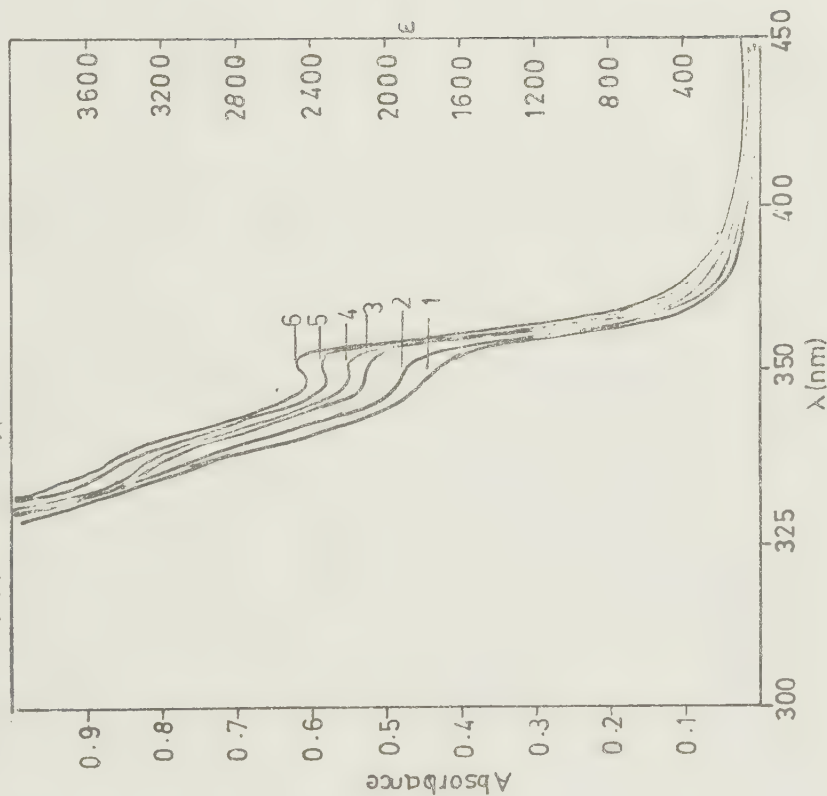


Figure 20

Kinetics of formation of $[\text{Pd}(\text{phen})_2]^{2+}$ at pH 2.

$C_{\text{Pd}} = 2.4995 \times 10^{-4} \text{ M}$, $C_{\text{Phen}} = 2.4999 \times 10^{-4} \text{ M}$

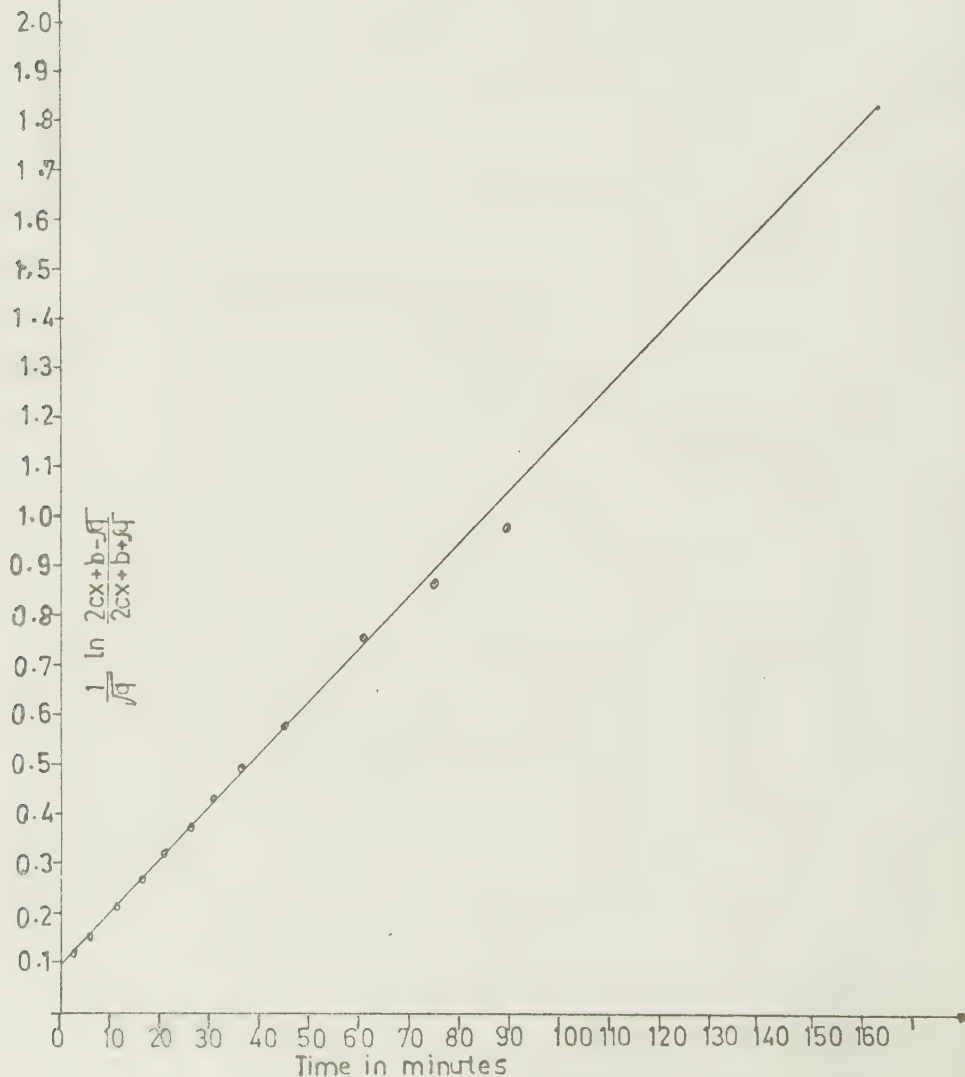


TABLE XI

H^+	$k_f (Ml^{-1} sec^{-1})$
0.01	10.39
0.1	1.1
0.2	1.0
0.5	1.02
1.0	1.3

From the above table it can be seen that the rate of formation of the bis complex at pH 2 is not dependent on the hydrogen ion concentration but the reaction at pH 2 is 10 times faster.

Substitution reactions of both square planar palladium (II) and platinum (II) have been known to take place via SN_2 mechanism i.e. both the complex and the reagent take part in the rate determining step. The formation of the bis complex also falls into the same category. The complexes of palladium (II) unlike those of platinum (II) (rate of Pd (II) reactions 10^5 times that of Pt (II)) have been generally found to be formed too fast to be followed by ordinary techniques. But in recent years a large number of kinetic work has been carried out with sterically hindered Pd (II) complex. The rate of reactions of $[Pd(Et_4dien)X]^+$ is one such example.

Table (XII) gives the rate found for the reaction of $[Pd(Et_4dien)(H_2O)]^{2+} + X^-$. The table also gives the rates of formation of $Pd(phen)Cl_2$ from $[PdCl_4]^{2-}$ studied by Rund.

TABLE XII

$[Pd(Et_4dien)(H_2O)]^{2+} + Y^-$	$[PdCl_4]^{2-} + A$
Y^- $k_2 M^{-1} sec^{-1}$	A k_2 pH
$\mu = 0.5 \quad Cl^-$ 2.47	phen 3.8 2
	phen 3.89 3.9

The rate constants as such can not be strictly speaking used for comparison since the methods used to calculate them are not quite the same. Nevertheless the magnitude of these constants are an indication of the slowness of the reactions when compared to the reactions of $[\text{Pd}(\text{dien})\text{X}]^+$ which are over in less than a second ³⁶ whereas the bis phenanthroline formation at pH 2 took a few hours for completion. Hence it is seen that the low constant for the stability for the bis (phenanthroline) complex is manifested in its slow rate of formation.

Kinetic measurements were also carried out for the formation of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ from $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ and phen. Since the ethylenediamine molecule is more flexible than the phenanthroline molecule it was thought that the rate of a formation of the mixed ethylenediamine-phenanthroline complex would be faster than the bis(phenanthroline) complex.

For the kinetic study, $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ was prepared from $\text{Pd}(\text{en})\text{Cl}_2$ by reacting the latter with silver nitrate solution and filtering off the precipitated silver chloride. The solution was tested for the possible presence of chloride ions since even a trace amount of Cl^- would result in the precipitation of $\text{Pd}(\text{phen})\text{Cl}_2$. To the acidified solution (pH 2), phenanthroline (at the same pH) was added in the stoichiometric ratios of 1:1, 1:2 and the kinetics of formation followed by measuring the spectra in the region 300-400 nm as a function of time. Figure (21) shows a typical kinetic run. The spectra of $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ was measured in the absence of added phenanthroline and compared with the spectrum obtained by L. Rasmussen and C.K. Jørgensen ¹⁸ and the two were found to be identical. Since ξ of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ and phenH^+ have previously been measured, the concentrations of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ can be calculated. The rate constants were determined in the same way as described for the formation of bis(phenanthroline) palladium (II) complex. Figure (22) shows the second order plot for different ratio of phenanthroline to $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ ion. The constant obtained at pH 2 was $0.85\text{M}^{-1}\text{sec}^{-1}$.

The rate of formation of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ contrary to expectation was slower than the formation of $[\text{Pd}(\text{phen})_2]^{2+}$. The explanation for this unexpected result does not lie in a steric effect since this would be greater for $[\text{Pd}(\text{phen})_2]^{2+}$. The low value for $\text{Pd}(\text{phen})\text{en}^{2+}$ shows that

Figure 21

Absorption spectra for the formation of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ from $[\text{Pd}(\text{H}_2\text{O})_2]^{2+}$ and phenanthroline at pH 2 as a function of time.

$[\text{Pd}(\text{H}_2\text{O})_2]^{2+} = 5.0028 \times 10^{-4} \text{ M}$, $C_{\text{phen}} = 4.9999 \times 10^{-4} \text{ M}$

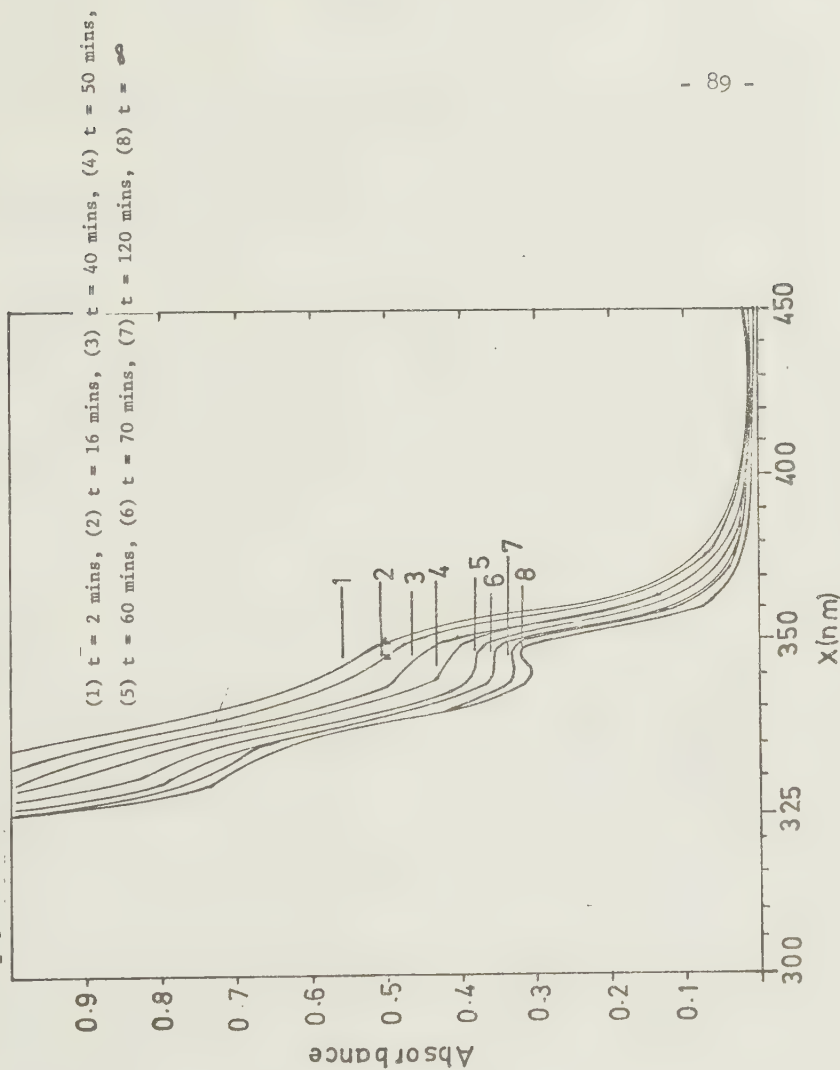
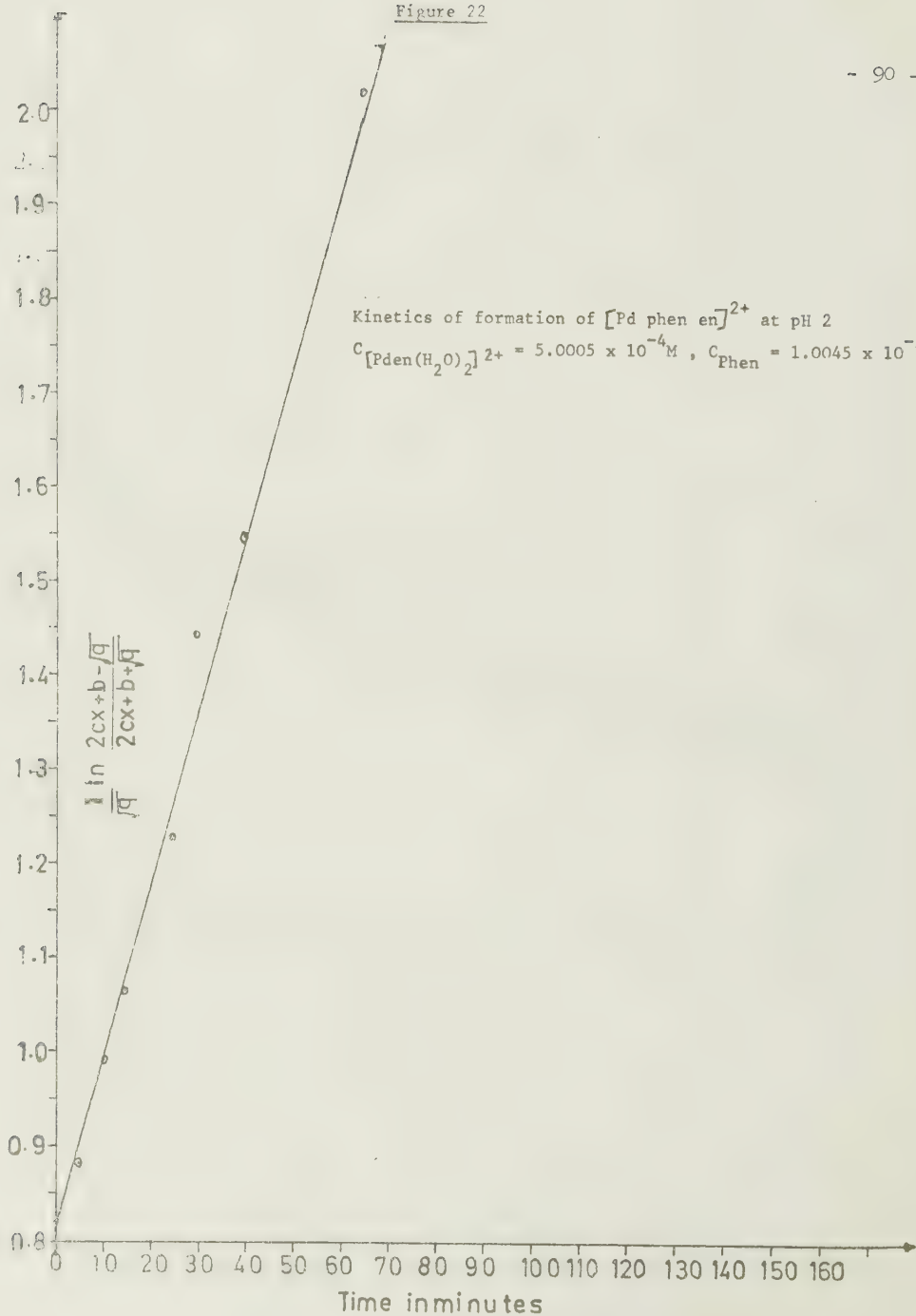


Figure 22

- 90 -

Kinetics of formation of $[\text{Pd phen en}]^{2+}$ at pH 2

$C_{[\text{Pden}(\text{H}_2\text{O})_2]^{2+}} = 5.0005 \times 10^{-4} \text{ M}$, $C_{\text{Phen}} = 1.0045 \times 10^{-3} \text{ M}$



even in this complex there is some steric hindrance although the stability constant of this is not different from the formation of $[\text{Pd}(\text{en})_2]^{2+}$.

Since a steric effect is present in both the complexes, the slower rate of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ formation might be attributed to the trans effect.

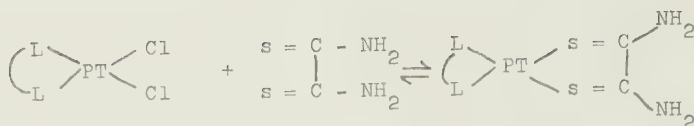
Dynamic Trans effect

The trans influence described in the previous chapter is a static effect and is reflected in the ground state properties of the complexes. The trans effect, on the other hand, is a kinetic effect and is the effect of a co-ordinated ligand A on the rate of substitution of the ligand opposite A. The static effect of ethylenediamine as reflected in the stability of the bond opposite it was shown to be higher than the phenanthroline ligand.

The static effect and the dynamic effect in most cases run parallel. The dynamic effect is a property not of the ground state but of the excited state or the transition state of the intermediate in the formation of the complexes. In solution, the trans effect will depend on the ability of the ligand in influencing the formation of the transition state. Since square planar reaction go via a 5 co-ordinate intermediate, stabilisation of this intermediate will enhance the formation of the final product. A ligand with a π bonding ability can participate in π bonding more effectively in the trigonal bipyramid intermediate than in the ground square planar state. The π bonding would involve overlap of filled electrons of the metal with the lowlying π orbital of the ligand and this would have the effect of lowering the charge density on the metal and thus would make it more accessible for attack by the incoming ligand.

Phenanthroline can participate in π bonding whereas ethylenediamine cannot and this difference might be responsible for the observed reaction rates.

This difference in the static and dynamic effect is shown in the reaction of $\text{cis } [\text{Pt}(\text{en})\text{Cl}_2]$ and in $[\text{Pt}(\text{phen})\text{Cl}_2]$ with dithiooxosulphate in methanol ³⁷.



The second order reaction rate together with the i.r. stretching frequencies are given in table XIII.

TABLE XIII

	$k_2 \times 10^2 (\text{M}^{-1} \text{sec}^{-1})$	$\nu(\text{Pt} - \text{Cl})$
$\text{Pt}(\text{en})_2\text{Cl}_2$	0.4	334,315
$\text{cisPt}(\text{bipy})\text{Cl}_2$	34	351,358

It is seen here $\text{Pt}(\text{bipy})\text{Cl}_2$ complex react 100 times faster than $\text{Pd}(\text{en})\text{Cl}_2$ although the opposite result would have been expected on the basis of bond strengths alone.

Kinetic study for the formation of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ from $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and en could not be studied quantitatively because the spectra of the two complexes are not very different. Since the kinetics of the other two complexes were studied at pH 2, for comparative purposes measurements of the formation must also be carried out at the same pH. The reaction of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ with en at pH 2 showed that the reaction time was comparable to those of $[\text{Pd}(\text{phen})_2]^{2+}$ and the formation of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ from $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$. It must be borne in mind that at pH 2, ethylenediamine is in the form of $[\text{enH}_2]^{2+}$ and whereas phenanthroline is only monoprotonated and thus has one position free to attack. It has been found for octahedral complexes that protonated ethylenediamine reactions are 50 times slower than unprotonated ones. Hence one might probably say that the formation of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ from $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+} + \text{en}$ is faster if account is taken of the factor of 50, but no positive conclusion can be drawn from it except to say that the reaction shows that there is some steric hindrance in such a complex.

Further proof of the nature of steric retardation in Pd (II) complex is obtained in the reaction of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ + 2,9 dimethyl phenanthroline. A qualitative observation (since quantitative measurements could not be carried out because of the resulting insoluble $[\text{Pd}(\text{phen})\text{dmp}]^{2+}$) showed that the formation of $\text{Pd}(\text{phen})\text{dmp}^{2+}$ as a pale pink precipitate was noticeably slow. The pink colour of the product is an indication of the nonplanarity of the two phenanthroline rings forming a pseudo 5 co-ordinate complex. .

Finally it must be said that equilibrium constants do not always point out the steric overcrowding of the complexes. The stability constant for the formation of $[\text{Pd}(\text{phen})\text{en}]^{2+}$ from $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ and en is comparable with the constant for the formation of $[\text{Pd}(\text{en})_2]^{2+}$ whereas the kinetics of formation indicate that in the former case there is some steric hindrance.

In the case of Cu (II) complexes a similar lack of correlation between steric hindrance and thermodynamic constant is obtained. The stability constants (log) for the formation of $[\text{Cu}(\text{en})_2]^{2+}$ from $[\text{Cu}(\text{en})]^{2+} + \text{en}$ and the formation of $[\text{Cu}(\text{bipy})\text{en}]^{2+}$ from $[\text{Cu}(\text{bipy})]^{2+} + \text{en}$ are very similar and are 9.16 and 9.15 respectively ⁴². The spectra of the complexes ³⁹ shows that there is steric overcrowding in the latter complex.

CHAPTER VI

SPECTRA OF PALLADIUM-PHENANTHROLINE COMPLEXES

The near ultraviolet spectra of pale yellow $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ (Figure 16), bright yellow $[\text{Pd}(\text{phen})(\text{OH})_2]$ and $[\text{Pd}(\text{phen})(\text{CH}_3)_3]^-$ solutions (Figure 23) are quite different.

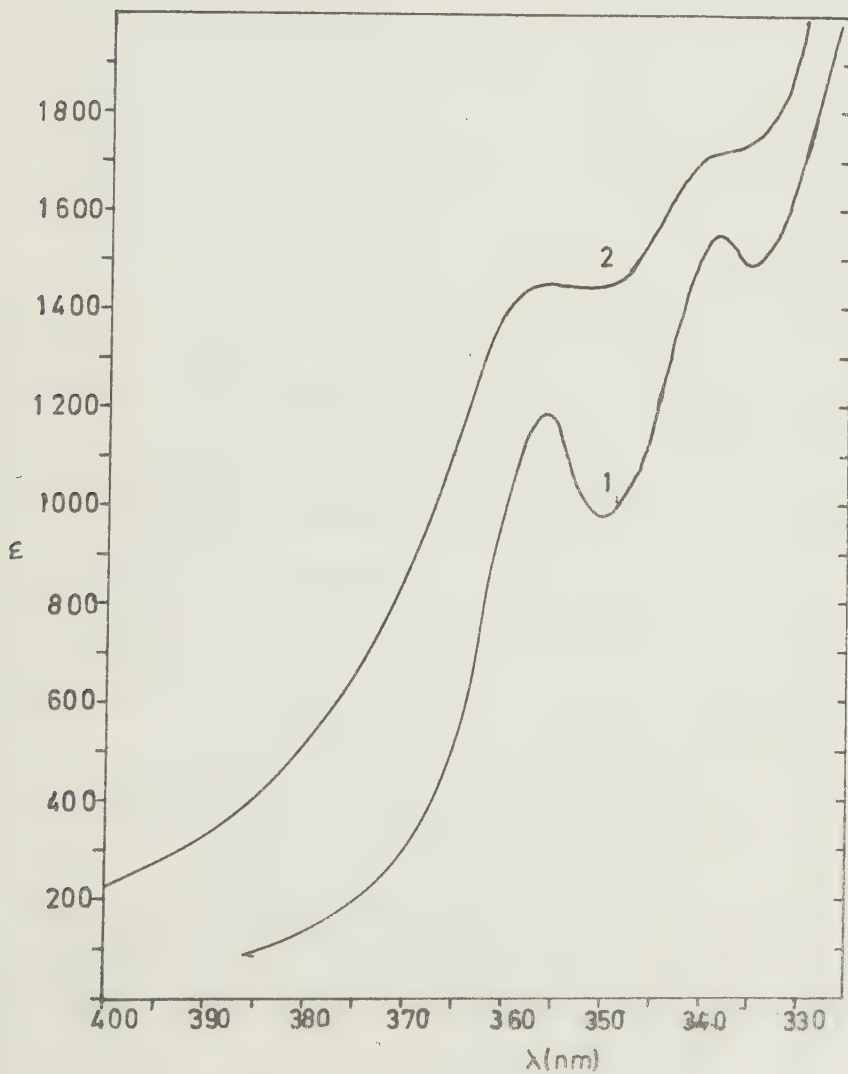
Palladium (II) complexes are known to form mainly square planar complexes. In theory there are three spins allowed d-d type transition viz $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$, $a_{1g}(\sigma^*) \rightarrow b_{1g}(\sigma^*)$ and $e_g(\pi^*) \rightarrow b_{1g}(\sigma^*)$. $[\text{PdN}_2\text{O}_2]$ chromophore should have an absorption band around 340 nm. Both the position and the intensity of the first absorption band (shoulder in the case of $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$) shows that this band is not due to a d-d transition. The intensity of the band is too low for a charge transfer of the type $M \rightarrow L$. Since phenanthroline and phenanthroline ion are known to have absorption maxima at 265 nm and 229 nm in the former and 272 nm, 225 nm and 206 nm in the latter, this band is not pure internal transition in the ligand. This band is probably due to a transition between ligand orbital of phenanthroline but with the orbitals being influenced due to the presence of slight interaction with metal orbitals since the band is sensitive to the ligands attached to the metal.

The change in spectra from the aquo to hydroxo complex with the maximum shifting to lower wave numbers and the intensity increasing conforms with the behaviour of aquo and hydroxo complexes of transition metal complexes. C.K. Jørgensen²¹ pointed out that in the case of palladium (II) the hydroxo complexes (of both $[\text{Pd}(\text{OH})_4]^{2-}$ and $[\text{Pd}(\text{dien})\text{OH}]^+$ are shifted towards higher wave numbers contrary to the spectrochemical series of ligands. Hence the observed conformity of the $\text{Pd}(\text{phen})(\text{OH})_2$ complex with the spectrochemical series is perhaps fortuitous.

The change in intensity in going from $[\text{Pd}(\text{phen})(\text{OH})_2]$ to $[\text{Pd}(\text{phen})(\text{OH})_3]^-$ (not following the same direction as that of aquo to dihydroxo) indicates that there is some structural change since otherwise there should be an increase in intensity. This might be due to the fact that $[\text{Pd}(\text{phen})(\text{OH})_3]^-$ is penta co-ordinate whereas both the

Figure 23

Absorption spectra of (1) $[\text{Pd}(\text{phen})(\text{OH})_3]^-$ ($[\text{Pd}(\text{phen})(\text{OH})_2]$ in 0.01M NaOH) and (2) $[\text{Pd}(\text{phen})(\text{OH})_2]$ in water.

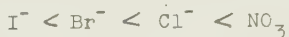


aquo and dihydroxo complexes have co-ordination four . This effect is similar to the pentammine effect observed in the case of Cu^{2+} with ammonia.

The spectrum of $[\text{Pd}(\text{phen})_2]^{2+}$ is shown in figure (16). The change in absorption towards shorter wave number and the increase in absorption is due to the steric effect of the two phenanthroline molecules making the molecule lose planarity. In the absence of any steric strain the absorption band should have been similar to that of $[\text{Pd}(\text{phen})\text{en}]^{2+}$. The distortion of the complex would lead to a mixing of orbitals and thus lead to an absorption band with a higher extinction coefficient at a lower wave number. The displacements of bands towards shorter wave numbers has been previously observed for $\text{Cu}(\text{II})$ complexes of phenanthroline⁴⁰ and mixed phenanthroline complex⁴¹. This change in absorption due to a steric effect is more striking in the case of mixed $[\text{Pd}(\text{phen})(\text{dmp})]^{2+}$ complex. Although the spectrum of this complex was not measured because of its low solubility in water, the formation of this complex can be observed by the change in colour from yellow $[\text{Pd}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ to pink $[\text{Pd}(\text{phen})(\text{dmp})]^{2+}$.

The dihalo complexes of $\text{Pd}(\text{phen})\text{X}_2$ were found to be insoluble in water but were found to be soluble in dimethyl sulphoxide.

Fig. (24, 25) show the spectra of $\text{Pd}(\text{phen})\text{Cl}_2$, $\text{Pd}(\text{phen})\text{Br}_2$, $\text{Pd}(\text{phen})\text{I}_2$ and $\text{Pd}(\text{phen})(\text{NO}_3)_2$ in dimethyl sulphoxide. It can be seen that the first maximum in spectra follows the spectro-chemical order i.e.



The big shift in the spectrum of $\text{Pd}(\text{phen})\text{I}_2$ is probably due to the fact that the observed band is a charge transfer band from the metal to the ligand.

The extinction coefficients are all higher than that observed in water perhaps due to the solvation effect not through the metal but through the ligand. In the case of halo complexes, halide ions were added to make sure that halide ions were not being partially replaced by dimethyl sulphoxide.

Figure 24

Absorption spectra of (1) $\text{Pd}(\text{phen})(\text{NO}_3)_2$ ($4.9489 \times 10^{-4} \text{ M}$) and
(2) $\text{Pd}(\text{phen})\text{Cl}_2$ ($4.9947 \times 10^{-4} \text{ M}$) in dimethylsulphoxide.

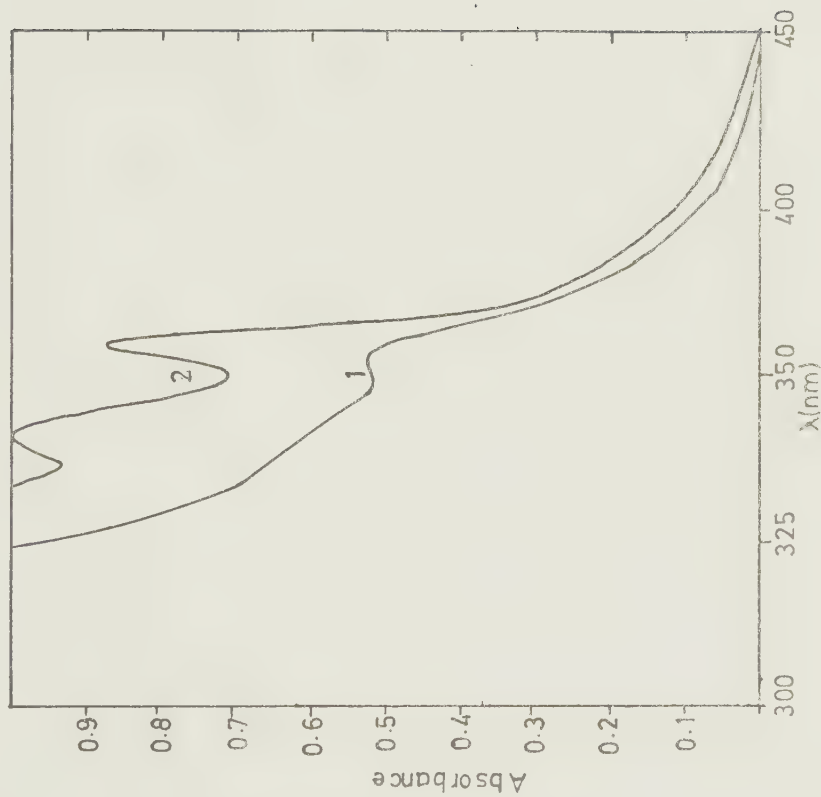


Figure 25

Absorption spectra of (1) $\text{Pd}(\text{phen})\text{Br}_2$ ($2.6025 \times 10^{-4} \text{ M}$) and
(2) $\text{Pd}(\text{phen})\text{I}_2$ ($4.9255 \times 10^{-4} \text{ M}$) in dimethyl sulphoxide.



Table XV gives the results of the spectra in dimethyl sulphoxide.

<u>TABLE XV</u>	<u>λ(nm)</u>	<u>ϵ</u>	<u>ν(kK)</u>
$\text{Pd(phen)(NO}_3)_2$	354	2000	28.4
Pd(phen)Cl_2	557.5	1780	27.9
Pd(phen)Br_2	360	3230	27.8
Pd(phen)I_2	478	983.	20.8

CONCLUSION

The stability constants have been measured for the two ligands bound to monophenanthroline palladium (II) complex. They are tabulated below.

	$\log K_1$	$\log K_2$	$\log K_3$
$[\text{Pd}(\text{phen})(\text{NH}_3)_2]^{2+}$	7.45	6.3	
$[\text{Pd}(\text{phen})(\text{OH})_3]^-$	10.7	8.1	4.4
$[\text{Pd}(\text{phen})(\text{py})_2]^{2+}$	7.02	6.18	
$[\text{Pd}(\text{phen})_2]^{2+}$	9.4		
$[\text{Pd}(\text{phen})\text{en}]^{2+}$	17.8		
$\text{Pd}(\text{phen})\text{Cl}_2$	7.0		
$\text{Pd}(\text{phen})\text{Br}_2$	8.7		

The stability constants show that the presence of strong Pd - phen bond does not appreciably lower the bond strengths of the ligands opposite to it. The formation constants of the pyridine complex and in fact the high affinity of palladium for phenanthroline emphasises the soft acid property of palladium (II) ion.

The most surprising result has been the formation of five co-ordinate $[\text{Pd}(\text{phen})(\text{OH})_3]^-$ ion in excess hydroxide ion. This formation has been attributed to the electron withdrawing nature of the phenanthroline ligand. This hypothesis could be tested on system similar to phenanthroline; dimethyl phenanthroline should act in a similar way but because of it's low solubility, this hypothesis could not be tested.

Steric hindrance has been shown to be responsible for both the thermodynamic (low stability constant) and the kinetic property (slow reaction) of $[\text{Pd}(\text{phen})_2]^{2+}$ complex. The formation constant of Pd - dmp bond in $[\text{Pd}(\text{phen})\text{dmp}]^{2+}$ should be even smaller than the second constant of $[\text{Pd}(\text{phen})_2]^{2+}$ ion but this could not be verified because of the exceedingly low solubility of this complex.

Provided that a weak polar solvent can be found that will dissolve $\text{Pd}(\text{phen})(\text{Cl}_2)$, one should be able to observe the formation of $[\text{Pd}(\text{phen})(\text{Cl}_3)]^-$ in an excess of chloride ions.

It is hoped that further research on palladium phenanthroline system, provided a suitable solvent can be found, will be carried out to determine the effect of substitution in phenanthroline on the stability of the ligands opposite to it.

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